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BIOGENIC VOLATILE ORGANIC COMPOUND (VOC) EMISSIONS FROM BOREAL DECIDUOUS TREES AND THEIR ATMOSPHERIC CHEMISTRY

Hannele Hakola

DISSERTATION

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Abstract

Plants emit various kinds of volatile organic compounds (VOC) into the atmosphere. The amount of biogenic VOCs is estimated to surpass the anthropogenic emissions, although emission rates from many of the plant species are yet unknown. The accurate estimates of the emissions of the biogenic hydrocarbons are needed because they have an important effect on atmospheric chemistry. They are highly reactive towards hydroxyl and nitrate radicals and ozone and in the presence of nitrogen oxides they contribute ozone and aerosol formation.

In the first part of the study the volatile organic compound (VOC) emission rates of boreal deciduous trees were measured. *Populus tremula* and *Salix phylicifolia* were isoprene emitters and *Betula* species emitted monoterpenes. The VOC emissions showed seasonal variations. All of the tree species studied emitted monoterpenes soon after budbreak. These emissions declined, however, in a few days and they are likely residuals from buds. *Populus tremula* and *Salix phylicifolia* initiated isoprene emission about two weeks after the budbreak, but more time (4-5 weeks) was needed for the increase of the monoterpene emissions from *Betula* species. Monoterpene emission rates from *Betula* species were highly variable. The genetic origin affected the emission rates of the *Betula pubescens.* The main monoterpenes emitted from *Betula* species were *cis*- and *trans*-ocimenes and sabinene, *Betula pubescens* emitted also linalool and sesquiterpenes in addition to monoterpenes. Linalool emissions were highest early summer. VOC emissions were highly dependent on temperature, and isoprene and at least some of the monoterpenes were also dependent on light intensity. Physical disturbance of *Betula pubescens* caused high emissions of 3-hexenylacetate, 3-hexen-1-ol, 1-hexanol and 2-hexenal, but did not affect monoterpene emission rates.

In the second part of the study, products formed from the gas-phase reactions of hydroxyl radical and ozone with monoterpenes were studied. The reactions were carried out in a Teflon chamber and products were then collected onto polyurethane foam adsorbents. Samples were then extracted, products separated using HPLC and identified by ^{1}H NMR. The products identified were those expected from the decomposition of the double bond after the addition reaction to the double bond. Generally, monoterpenes that have double bond in the ring produced keto-aldehydes and monoterpenes that have double bond external to the ring produced ketones. Product yields were at most 50%, so most of the products were not accounted for.

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PAPERS INCLUDED IN THE THESIS

I: Hakola Hannele, Janne Rinne and Tuomas Laurila, 1998. The hydrocarbon emission rates of Tea-leafed willow (*Salix phylicifolia*), Silver birch (*Betula pendula*) and European aspen (*Populus tremula*). *Atmospheric Environment, 32,* 1825-1833.

II: Hakola H., Laurila T., Lindfors V., Hellén H. Gaman A., and Rinne J., 2001. Variation of the VOC emission rates of birch species during the growing season. *Boreal Environment Research*, 6, 237-249.

III: Hakola H., Laurila T., Rinne J., and Puhto K., 2000. The ambient concentrations of biogenic hydrocarbons at a Northern European, boreal site. *Atmospheric Environment*, 34, 4971-4982.

IV: Hakola H., Shorees B., Arey J. and Atkinson R., 1993. Product formation from the gas-phase reactions of OH radicals and O_3 with beta-phellandrene. *Environmental Science and Technology 27*, 278-283.

V: Hakola H., Arey J., Aschmann S. and Atkinson R., 1994. Product formation from the gas-phase reactions of OH radical and O_3 with a series of monoterpenes. *Journal of Atmospheric Chemistry 18*, 75-102.

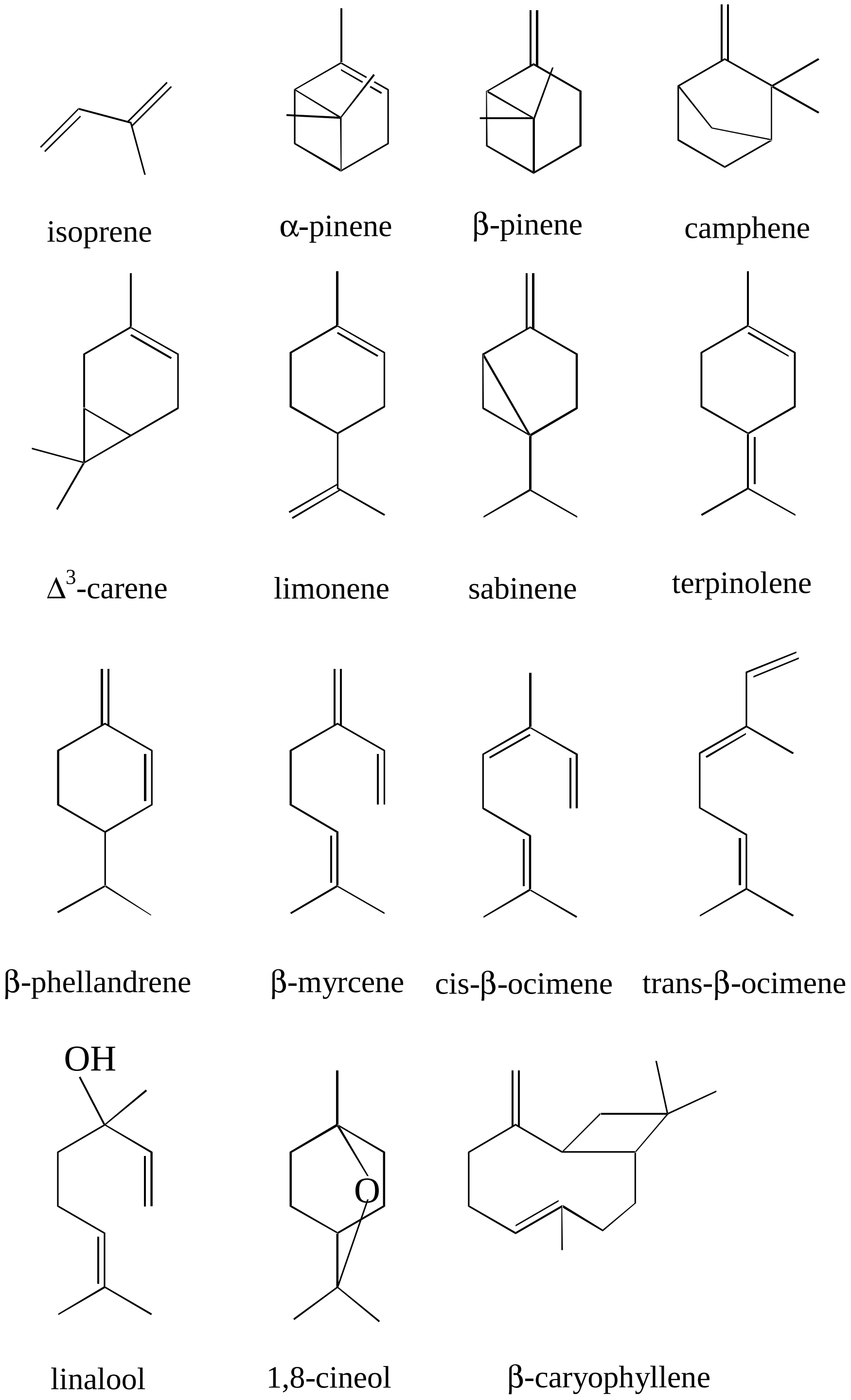
CONTENTS

1. INTRODUCTION

Plants emit various kinds of volatile organic compounds (VOC) into the atmosphere. These compounds consist of alkenes, aldehydes, ketones, esters, ethers, alcohols and acids (*Arey et al., 1991 a,b, 1995; Isidorov, 1994; Winer et al., 1992; Kesselmeier & Staudt, 1999*). Of great importance is a group of compounds called isoprenoids or terpenoids consisting of isoprene (C_5H_8), monoterpenes (two isoprene units) and sesquiterpenes (three isoprene units). Usually they are characterised as volatile, poorly water-soluble and very reactive compounds with a strong scent. The structures of some terpenoids and common oxygen-containing compounds, also considered to belong to the terpenoids group, are in Figure 1.

Monoterpenes are emitted from plants for a variety of reasons, including defence against insects and other herbivores and attraction of pollinators and enemies of herbivores (*Fall*, 1999). The reason for isoprene emission is still not quite clear. *Singsaas et al*. (1997) suggested that the emission of isoprene benefits plants by increasing their thermotolerance.

The amount of biogenic terpenoid emissions is estimated to exceed the amount of anthropogenic VOC emissions. *Müller et al.* (1992) gave the amount of global anthropogenic VOC emissions as 149 Tg/year (technological sources and biomass burning), while according to *Guenther et al*. (1995) the amount of global biogenic VOC emissions is estimated to be about 1150 Tg (C)/year, composed of 44% isoprene, 11% monoterpenes, 22.5% other reactive VOC (defined as compounds with a lifetime of less than one day) and 22.5% other VOC (lifetimes longer than one day). Finland is a densely-forested country and here



isoprene α-pinene β-pinene camphene

Δ^3-carene limonene sabinene terpinolene

β-phellandrene β-myrcene cis-β-ocimene trans-β-ocimene

linalool 1,8-cineol β-caryophyllene

Figure 1: The structures of some of the terpenoid compounds emitted by vegetation

too the annual biogenic hydrocarbon emissions surpass the anthropogenic VOC emissions. Annual anthropogenic VOC emissions in Finland are estimated to be 193 kilotonnes (*Mroueh*, 1994) whereas the first estimates of biogenic emissions calculated by *Lindfors & Laurila* (2000) reach 318 kilotonnes per annum.

The chemistry of the atmosphere is strongly influenced by biogenic VOC emissions due to their magnitude and high reactivity towards the OH radical, NO_3 and ozone. During the past two decades a lot of effort has been put on the identification and quantification of oxidation products resulting in these reactions. Product studies under atmospheric conditions have faced difficulties due to analytical problems in detecting multifunctional groups, as well as the lack of commercial standards for the anticipated products. Product and mechanistic studies have recently been reviewed by *Calogirou et al.* (1999), *Fuentes et al*. (2000) and *Atkinson* (2000).

The oxidation process of isoprene and monoterpenes is important because it can produce ozone in the presence of nitrogen oxides (mainly emitted from combustion sources). Ozone is a reactive oxidant that is harmful to vegetation and animals. In addition to their ozone-forming potential, monoterpenes and especially sesquiterpenes have a potential for forming secondary organic aerosols (*Hoffmann et al.*, 1997). New particle formation in a forested area has been reported (*Mäkelä et al.*, 1997); these new particles are most probably caused by interaction of organic acids produced by the photo-oxidation of terpenes with other organic or inorganic species present in the atmosphere (*Kavouras et al*., 1998).

The first objective of this work was to measure terpenoid emission rates from boreal deciduous trees for the VOC emission inventory purposes. Deciduous trees were chosen, because available data concerning boreal deciduous species were almost absent. Boreal coniferous trees have been studied earlier by *Janson* (1993), *Schürman et al*., (1993), *Janson & de Serves* (2001) and *Janson et al*. (2001). Accurate estimates of the biogenic VOC emissions are needed for the development of efficient ozone control strategies. They are also essential in the evaluation of the contribution of biogenic VOCs to atmospheric aerosol formation. As a result of these measured emission rates the first biogenic VOC emission estimates in Finland have been published (*Lindfors & Laurila*, 2000; *Lindfors et al.*, 2000). The ambient concentrations of biogenic VOCs were measured in order to validate emission rate measurements. They were considered to reveal possible new VOC sources, to give more information about the seasonality of the emission rates and to describe the effect the biogenic VOCs have on photochemistry.

In the atmosphere, monoterpenes react with hydroxyl and nitrate radicals and ozone. While reaction rate coefficients for many of these reactions have been determined (*Atkinson*, 1994), there are not much data available concerning the products of these reactions. The second objective of the study was to identify and quantify the main products formed in the reactions with ozone and OH radical and monoterpenes. Most of the products identified earlier were tentative based on mass spectra alone (*Arey et al.*, 1990). In this work an experimental technique was developed to allow sufficient amounts of the products formed in these reactions to be collected and purified for complete spectroscopic identification. The only quantitative yield data earlier was from the reactions of α-pinene and β-pinene with OH radical and ozone *(Hatakeyama* *et al.*, 1989, 1991) and the OH radical reactions with α-pinene, β-pinene, limonene, myrcene, sabinene, terpinolene and Δ^3-carene (*Arey et al.*, 1990).

Papers I and II deal with emission rate measurements from *Betula pendula*, *Betula pubescens*, *Populus tremula* and *Salix phylicifolia*. Special attention has been paid to the seasonal variation of the emission rates. Paper III presents ambient concentrations of biogenic VOCs in a boreal, forested site. Papers IV and V deal with the chemistry of monoterpenes in air. Paper IV presents a method of producing, collecting and separating products formed in monoterpene reactions with O_3 and the OH radical in a chamber experiment for complete spectroscopic analysis. This technique was then applied in paper V to several monoterpenes and some of the products formed in these reactions were identified and quantified.

Several other persons have made important contributions to these papers. J. Rinne arranged the temperature, radiation, relative humidity and CO_2 measurements in the emission-rate measurements. In papers IV and V, the author’s contribution was to develop a method for the separation of products and to conduct the spectroscopic identification while the quantification was conducted by Professors Arey and Atkinson.

2. REACTIONS OF MONOTERPENES IN AIR

Isoprene and monoterpenes are alkenes and their gas-phase atmospheric reactions are generally analogous to those of other alkenes such as propene. Many of the mechanistic studies have been conducted on small alkenes but the reactions of monoterpenes can be more complicated for example due to strained rings in some monoterpene structures. Isoprene and monoterpenes are highly reactive towards the OH and NO_3 radicals and ozone. In the troposphere OH radicals are formed mainly due to the photolysis of O_3 in the presence of water vapour according to reactions (1)-(4).

$$O_3 + h\nu \longrightarrow O_2 + O\,(^1D) \qquad (1)$$

$$O\,(^1D) + M \longrightarrow O\,(^3P) + M\ (M{=}O_2, N_2) \qquad (2)$$

$$O\,(^3P) + O_2 + M \longrightarrow O_3 + M \qquad (3)$$

$$O\,(^1D) + H_2O \longrightarrow 2\,OH \qquad (4)$$

The excited $O(^1D)$ atoms are either deactivated to ground state oxygen, $O(^3P)$, in collisions with air molecules, or react with water vapour to generate OH radicals. Hydroxyl radicals are formed in this process only during daylight. At night they can be produced in the reactions between alkenes and O_3 and this source can also be significant (*Atkinson et al.*, 1992).

Ozone is produced in the troposphere by photolysis of NO_2 (*National Research Council*, 1991).

$$NO_2 + h\nu \longrightarrow NO + O\,(^3P) \qquad (5)$$

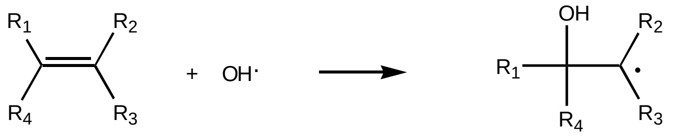
$$O\,(^3P) + O_2 \longrightarrow O_3 \qquad (6)$$

On the other hand, ozone rapidly oxidizes the nitrogen oxide molecule formed in reaction (5) back to nitrogen dioxide.

$$O_3 + NO \longrightarrow NO_2 \qquad (7)$$

In the atmosphere these three reactions are in photochemical balance, unless there are other oxidants in addition to ozone to convert NO to NO_2. In this case reactions (5) and (6) may lead to net ozone production.

The hydroxyl radicals mainly react with atmospheric alkenes by addition to the double bond. The atmospheric oxidation reactions of biogenic (and also anthropogenic) hydrocarbons with OH radicals produce organic peroxy radicals ($RO_2^{\cdot}$) and hydrogen peroxy radicals ($HO_2^{\cdot}$) (reactions 8-13). These radicals readily oxidize NO to NO_2, thus leading to ozone production.



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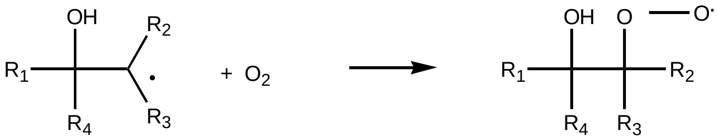

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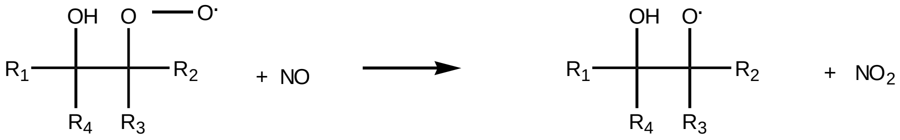

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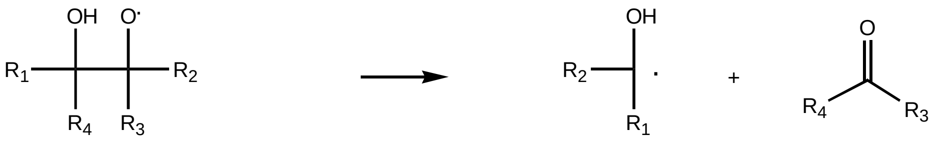

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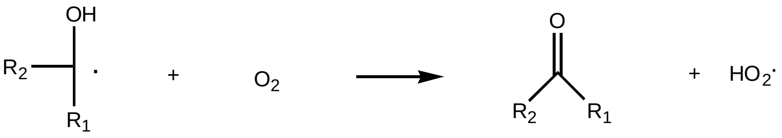


(12)

$$HO_2^{\cdot} + NO \longrightarrow OH^{\cdot} + NO_2 \qquad (13)$$

In reactions (5)-(13) 2 NO molecules are oxidized thus leading to the production of two ozone molecules for each reacted alkene molecule. In clean air with very low NO_x concentrations, the number of NO molecules is not sufficient for reactions (10) and (13) to be effective. In this case, the peroxy radicals can combine (reactions 14 and 15) and no ozone is formed, or they can react with ozone, thus leading to ozone destruction (reactions 16 and 17).

$$HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O_2 + O_2 \tag{14}$$

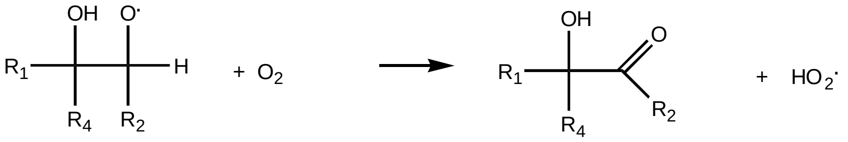
$$RO_2^{\cdot} + HO_2^{\cdot} \longrightarrow ROOH + O_2 \tag{15}$$

$$OH^{\cdot} + O_3 \longrightarrow HO_2^{\cdot} + O_2 \tag{16}$$

$$HO_2^{\cdot} + O_3 \longrightarrow OH^{\cdot} + 2\,O_2 \tag{17}$$

Whether ozone is destroyed or produced in the troposphere depends on the rates of reactions (14)-(17) (*Chameides et al.*, 1992; *Atkinson*, 2000). To arrive at efficient ozone control strategies, the emissions of anthropogenic and biogenic VOCs, as well as the NO_x emissions have to be assessed.

The β-hydroxyalkoxy radical produced by the reaction (10) has three possible reaction pathways: decomposition, reaction with molecular oxygen or isomerization (*Atkinson*, 2000). Decomposition (reaction 11a) produces a hydroxyalkyl radical that can react with molecular oxygen (12). The decomposition mechanism thus results in two aldehyde/ketone molecules (reactions 11a and 12) or, as with bicyclic monoterpenes, the ring containing the double bond can break, leading to a monocyclic dicarbonyl product. Decomposition is the most important pathway for the smaller alkenes (*Atkinson*, 1994), but for the larger alkenes (C_6-C_8) the isomerization (reaction 11c) dominates (*Eberhard et al.*, 1995; *Kwok et al.*, 1996). The β-hydroxyalkoxyradical isomerizes to a dihydroxyalkylradical that continues to react with molecular oxygen and NO to form dihydroxycarbonyl compounds (*Kwok et al.*, 1996). β-Hydroxyalkoxyradical can also react with molecular oxygen to produce hydroxycarbonyls (reaction 11b). So far not many hydroxycarbonyl compounds have been identified, but *Aschmann et al.* (2000) detected a β-hydroxycarbonyl product after an α-pinene reaction with an OH radical in the absence of NO, while in the presence of NO decomposition was the main mechanism.



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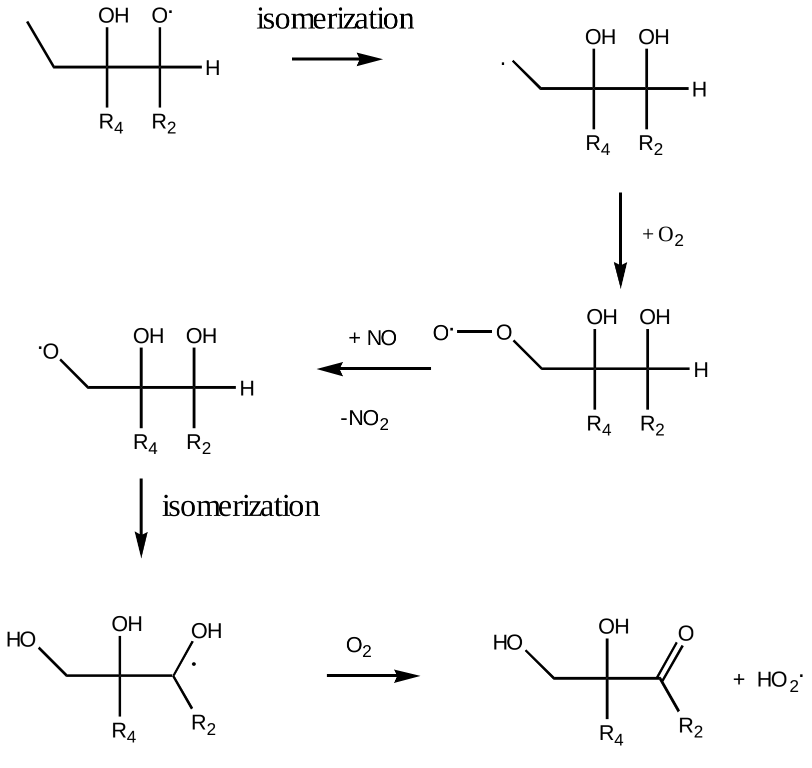

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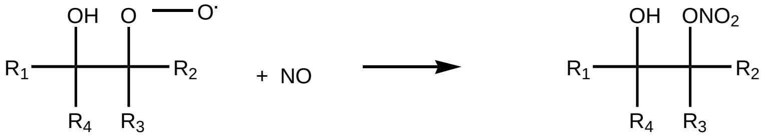
In very polluted air NO can combine with a β-hydroxyalkylperoxy radical forming β-hydroxynitrate instead of reaction 10. However, this reaction is of minor importance.



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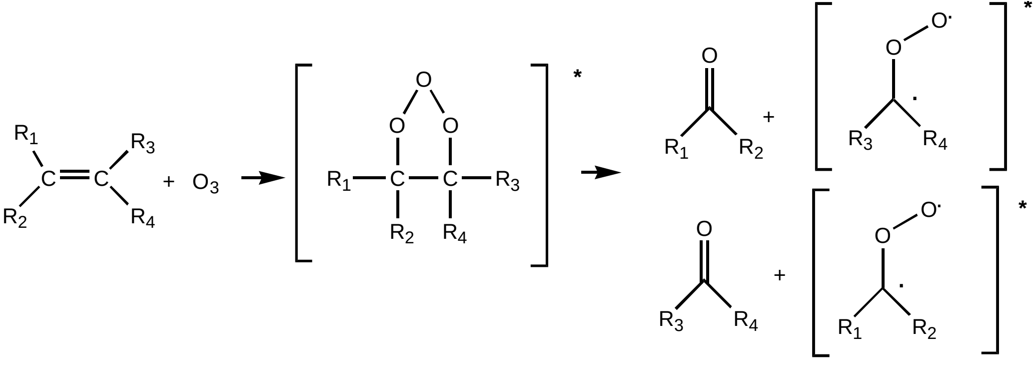
Muthuramu et al. (1993) have determined the yield of 2-nitrooxy-3-hydroxybutane formation from OH radical reaction with *cis*-2-butene in the presence of NO, to be 0.037.

Besides the addition to the double bond, hydroxyl radical can also react with alkenes by abstracting a hydrogen atom. Generally, abstractions are of minor importance (*Atkinson*, 1994), but sometimes they are not negligible; for example 20% of 1-octene was found to react with OH radical by hydrogen abstraction, while 80% reacted by the addition mechanism (*Paulson & Seinfeld*, 1992).

The oxidation of monoterpenes by O_3 also starts with an addition to the double bond. Contrary to the oxidation by hydroxyl radical this reaction proceeds both during the day and at night. The mechanism produces two sets of carbonyl and a biradical (*Atkinson*, 2000).



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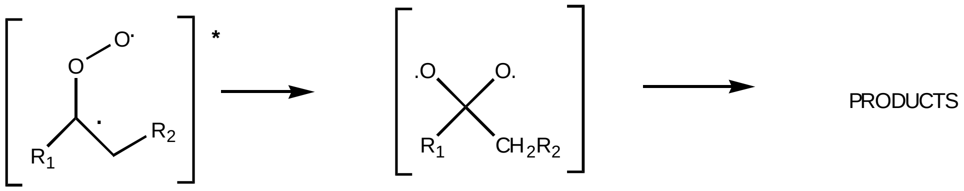
The biradicals formed in the ozone reaction can be collisionally stabilized or decompose in a number of ways (*Alvarado et al.*, 1998; *Atkinson* 2000).



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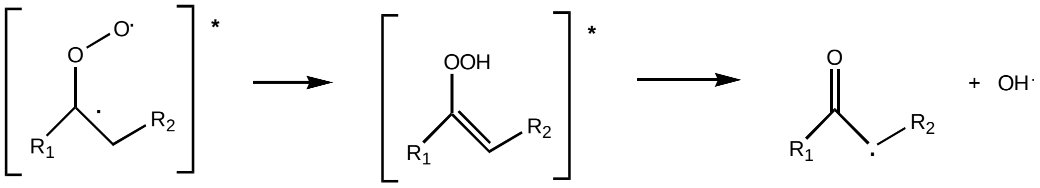

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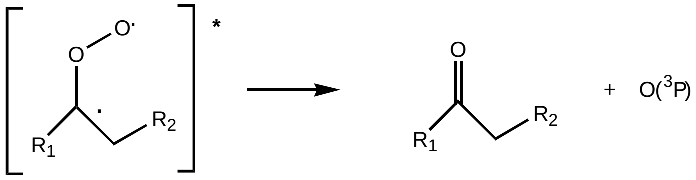

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The products arising from the biradicals during monoterpene oxidation are not completely understood. However, it is known that the reaction of ozone with alkenes produces OH radicals (*Atkinson et al.*, 1992) often in large yields (*Paulson et al.*, 1998). Reaction 21 is the main pathway at least for α*-pinene (Alvarado et al.*, 1998) while the reaction producing an oxygen atom (reaction 22) is of minor importance.

The excited biradical can also react with water vapour producing organic acids (*Horie et al.*, 1994; *Neeb et al.*, 1997). Any alkene with terminal double bonds like isoprene, sabinene, limonene and β-pinene are all capable of forming acids in varying degrees (*Horie et al.*, 1994).

$$^{\cdot}\mathrm{CH2OO}^{\cdot} + \mathrm{H_2O} \longrightarrow \mathrm{HOCH_2OOH} \longrightarrow \mathrm{HCOOH} + \mathrm{H_2O} \qquad (23)$$

Organic acids produced in the reactions of ozone with monoterpenes are considered to be important elements in gas-to-particle conversion (*Hoffmann et al.*, 1997; *Christoffersen et al.*, 1998; *Kavouras et al.*, 1998; *Jang & Kamens*, 1999). Several organic acids have been detected in ambient air samples, *e.g.* norpinic acid from α-pinene and pinic acid from β-pinene oxidation reactions were identified in the aerosol phase samples taken in Canada and California (*Yu et al.*, 1999).

In addition to ozone and OH radicals, alkenes also react with nitrate radicals. Nitrate radicals in the troposphere are formed from NO and NO_2 with ozone.

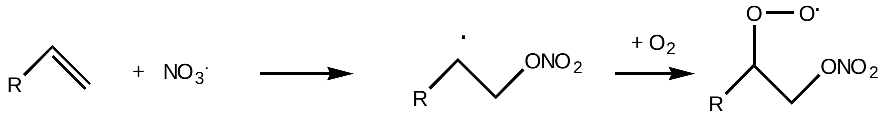
$$\mathrm{NO}^{\cdot} + \mathrm{O_3} \longrightarrow \mathrm{NO_2}^{\cdot} + \mathrm{O_2} \qquad (24)$$

$$\mathrm{NO_2}^{\cdot} + \mathrm{O_3} \longrightarrow \mathrm{NO_3}^{\cdot} + \mathrm{O_2} \qquad (25)$$

$$\mathrm{NO_3}^{\cdot} + h\nu \begin{array}{l} \longrightarrow \mathrm{NO_2}^{\cdot} + \mathrm{O}\,(^3\mathrm{P}) \\ \longrightarrow \mathrm{NO}^{\cdot} + \mathrm{O_2} \end{array} \qquad (26)$$

Nitrate radicals decompose rapidly in sunlight (reaction 26), and therefore reactions of NO_3 and alkenes are efficient only at night (*National Research Council*, 1991).

Also nitrate radical reactions are addition reactions and proceed similarly to the hydroxyl radical reactions (*Wayne et al.*, 1991; *Skov et al.*, 1992) with the exception that the nitrooxyalkyl peroxy radical reacts with NO_2 rather than NO.



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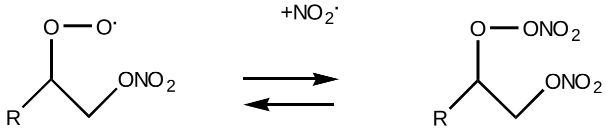
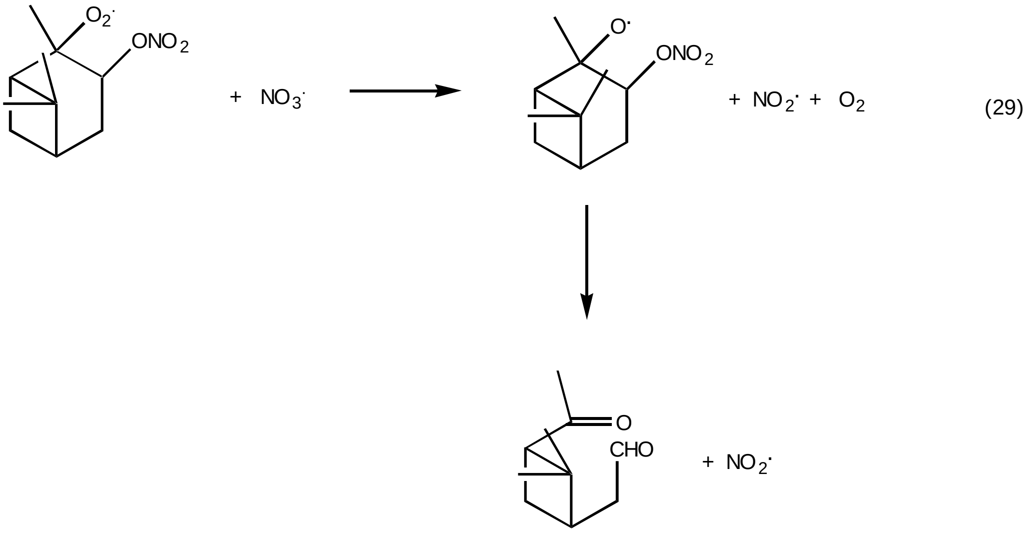


(28)

This is because the NO concentrations are low in the presence of nitrate radicals (nitrate radicals react rapidly with NO producing NO_2). The formed peroxynitrates are thermally unstable and in a cold climate peroxynitrates can serve as a reservoir for peroxides and NO_2. Depending on their lifetimes, they can transport nitrogen oxides for considerable distances.

The reaction mechanisms of alkenes and nitrate radical are not fully understood and not many products arising from these reactions have been identified due to analytical difficulties. *Wängberg et al.* (1997) studied the α-pinene reaction with the nitrate radical and found pinonaldehyde to be the main reaction product (62 % yield). Other identified products were: pinane epoxide, 3-hydroxypinan-3-nitrate and 3-oxopinan-2-

nitrate. The large fraction of pinonaldehyde found in the study indicates that although nitrate radical adds to the double bond the nitrate is later released. They propose a tentative mechanism leading to pinonaldehyde (reaction 29) from peroxyradical formed in reaction 27.



Contrary to α-pinene, β-pinene and Δ^3-carene were found to produce mainly nitrates (60-70 %) with carbonyl yields of about 10 % and 20-30 % for β-pinene and Δ^3-carene, respectively (*Hallquist et al.*, 1999).

For many of the terpenoid compounds the reaction rate coefficients with the OH and NO_3 radicals and ozone have been determined (*Atkinson*, 1994); the most common compounds are shown in Table 1 together with their estimated atmospheric lifetimes. The calculated lifetimes generally vary from a few minutes to hours.

Table 1: Rate constants for the gas-phase reactions of OH and NO_3 radicals and O_3 with isoprene and some of the terpenes and their calculated tropospheric lifetimes with respect to these reactions (mean concentrations assumed $[O_3]= 7*10^{11}$ molecules cm^{-3} (30 ppb), $[OH^{\cdot}]=5*10^5$ molecules cm^{-3} (0.02 ppt) and $[NO_3]= 1*10^8$ molecules cm^{-3} (4 ppt). 30 ppb is the mean ozone concentration observed in Finland (*Air Quality measurements 2000*), 4 ppt was the upper limit obtained for the mean night-time NO_3 concentration in an eucalyptus forest in rural Portugal (*Gölz et al.*, 2001) and $OH^{\cdot}$ midday average peak concentration for sunny conditions is $(1-10)*10^5$ molec. cm^{-3} (*Finalyson-Pitts & Pitts*, 1986). The rate constants are from *Atkinson* (1994) except those for β-caryophyllene, which are from *Shu & Atkinson* (1995).

Biogenic VOC	Rate constants (cm^3 $molecule^{-1}$ s^{-1})			Tropospheric lifetime for reaction with		
	$OH^{\cdot}$	$NO_3^{\cdot}$	O_3	$OH^{\cdot}$	$NO_3^{\cdot}$	O_3
Isoprene	$101*10^{-12}$	$6.78*10^{-13}$	$12.8*10^{-18}$	5.5 h	4.1 h	31 h
α-pinene	$53.7*10^{-12}$	$6.16*10^{-12}$	$86.6*10^{-18}$	10.3 h	27 min	4.6 h
β-pinene	$78.9*10^{-12}$	$2.51*10^{-12}$	$15*10^{-18}$	7.0 h	1.1 h	26 h
Δ^3-carene	$88*10^{-12}$	$9.1*10^{-12}$	$37*10^{-18}$	6.3 h	18 min	11 h
Camphene	$53*10^{-12}$	$6.6*10^{-13}$	$0.90*10^{-18}$	10.5 h	4.2 h	18 days
Limonene	$171*10^{-12}$	$1.22 *10^{-11}$	$200*10^{-18}$	3.2 h	13.7 min	2.0 h
Sabinene	$117*10^{-12}$	$1.0 *10^{-11}$	$86*10^{-18}$	4.7 h	16.7 min	4.6 h
β-ocimene	$252*10^{-12}$	$2.2 *10^{-11}$	$540*10^{-18}$	2.2 h	7.6 min	0.7 h
β-caryophyllene	$200*10^{-12}$	$1.9*10^{-11}$	$116*10^{-16}$	2.8 h	8.8 min	2.1 min

3. FACTORS AFFECTING BIOGENIC VOC EMISSION RATES

VOC emission rates do not remain constant throughout the growing season; they show considerable variation for example due to phenology, growth environment, environmental changes like temperature and light, nutrient and water availability. The factors affecting biogenic VOC emissions have been reviewed by (*Guenther et al.*, 1995 and *Kesselmeier & Staudt*, 1999).

Temperature and photosynthetically active radiation are the best-known variables affecting VOC emission rates in the short-term. Generally, monoterpenes are released into the atmosphere from storage pools, such as resin ducts or glands, as a function of temperature (*Tingey et al*., 1980). Some plants have been found to also emit monoterpenes that are not stored in the plant. These monoterpenes are emitted into the air directly after a light-dependent synthesis *e.g*. *Pinus densiflora* (*Yokouchi & Ambe*, 1984), *Picea abies* (*Shürmann et al*., 1993), *Quercus ilex* (*Loreto et al*., 1996, *Bertin et al*., 1997), sunflower and beech (*Schuh et al*., 1997) and *Pinus pinea* (*Staudt et al*., 1997, 2000).

Isoprene emission begins rapidly in light and is fully induced within 30 minutes (*Loreto & Sharkey*, 1990; *Monson et al.,* 1991). The emissions then increase with increasing PPFD (photosynthetic photon flux density), sometimes saturating at a certain PPFD level, such as 600-800 μmol m^{-2} s^{-1} with velvet beans (*Monson et al.*, 1991). *Harley et al.* (1997) measured isoprene emission dependence on PPFD using white oaks, and found no saturation at PPFD values approaching that of full sunlight.

Guenther et al., (1991, 1993, 1997) describe the light and temperature dependence of VOC emission rates by the algorithm

$$E = E_S * C_T * C_L \qquad \text{(eq. 1)}$$

where E is the measured emission rate and E_S is a standard emission potential (usually at a standard temperature of 30°C and a standard radiation of 1000 μmol m^{-2} s^{-1}). C_T

and C_L are the influence of temperature and light, respectively, and they are described according to equations 2 and 3

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1+\alpha^2 L^2}} \qquad \text{(eq. 2)}$$

$$C_T = \frac{\exp \dfrac{C_{T1}(T - T_S)}{RT_S T}}{0.961 + \exp \dfrac{C_{T2}(T - T_M)}{RT_S T}} \qquad \text{(eq.3)}$$

where α , C_{L1}, C_{T1}, C_{T2} and T_M are empirically-determined coefficients, R is a constant (=8.314 J K^{-1} mol^{-1}) and T and L are the temperature and light intensity of the isoprene emission measurement. Equation 4 is commonly used when describing the temperature dependence of stored monoterpene emission rates (*Tingey et al.*, 1980, *Lamb et al.*, 1987, *Guenther et al.*, 1993):

$$E = E_S * \exp(\beta(T - T_S)) \qquad \text{(eq. 4)}$$

where E is the monoterpene emission rate at temperature T (K), E_S is the monoterpene emission potential at a standard temperature T_S (K) and β (K^{-1}) is an empirical coefficient. *Guenther et al.* (1993) have suggested a β coefficient value of 0.09 K^{-1} for all monoterpene and plant species.

Other factors affecting VOC emissions have not been very clearly assessed. *Yokouchi & Ambe* (1984) and *Juuti et al.* (1990) concluded in their work that relative humidity did not affect monoterpene emission rates, whereas *Loreto et al.* (1996) found that relative humidity can affect the contribution of different monoterpenes to the total amount. Physical disturbance (e.g. rough handling of plants) can increase monoterpene emission rates, as shown by *Juuti et al*. (1990) with Monterey pine.

In addition to short-term changes, emission rates have also been found to vary in the longer term throughout the year. Emission of isoprene, for example, is highly dependent on the temperature the plant has experienced in the past (*Monson et al*., 1994; *Pétron et al*., 2001). Aspen trees growing in the Rocky Mountains in their natural environment do not initiate isoprene emission until six weeks after leaf emergence (*Monson et al.*, 1994). When non-emitting leaves are suddenly exposed to higher temperatures, isoprene emission rates increase. *Staudt et al*. (2000) studied the monoterpene emissions of *Pinus pinea* and found that the emission pattern as well as the emission potential changed during the year. The monoterpenes that were found to be dependent on light intensity were emitted only in the summer, whereas monoterpenes from resin ducts were released at any time and in any season as a function of temperature. So far there is not much emission rate data covering the whole growing season or the whole year.

4. MATERIALS AND METHODS

4.1. Measurement sites

The emission rate measurements were carried out at Ruotsinkylä, Vantaa, in southern Finland, at the station of the Finnish Forest Research Institute during the growing seasons of 1996, 1997 and 2000. During 1996 and 1997 measurements were carried out using a different tree each time. The measured trees were young, about 1-1,5 metres in height. In 1996 the trees measured were *Betula pendula* (silver birch), *Salix phylicifolia* (tea-leafed willow) and *Populus tremula* (European aspen). Because *Betula pendula* showed unexpected seasonal variations, the measurements were continued in 1997 in order to find out the time of onset of higher emission rates. The emission rates of *Betula pubescens* (downy birch) were also measured in 1997, and due to the irregularities in the emission rates in 1997, measurements on *Betula pubescens* were repeated in 2000 with two clones with different genetic origin. The Finnish Forest Research Institute numbers of the clones are E567 (Finnish origin) and D2472 (German origin). In order to find out if the variations were tree-to-tree or day-to-day variations, the trees used in 2000 were the same throughout the season. The clones were also older than trees used earlier, the diameter of the trees at a height of 1.5-meter being 22 and 24 cm.

The ambient air concentration measurements were carried out at Ilomantsi, in eastern Finland. Samples were collected about 1.5 m above the ground from an open field on the top of a hill called Pötsönvaara. The distance from the forest was about 100 m. The main tree species growing in the area was *Pinus sylvestris*, but *Picea abies*, *Betula pendula* and *Populus tremula* were also common. Close to the measuring site, were also *Salix* species. The landscape is mainly forested, but with some fields and cuttings. About 100 metres from the measuring site there was a house and a narrow road leading to the house from a larger road (about 500 metres) with a low traffic intensity (50-100 cars/day). Samples were collected 3-5 times a week during the growing seasons of 1997 and 1998.

4.2. The sampling and analysis of Volatile Organic Compounds (VOC) in air

The light hydrocarbons were collected as whole air samples in stainless steel canisters whose inner surfaces were passivated by a covering of chrome-nickel oxide. The canisters used in this work were evacuated prior to taking to a sampling site. At the site the canisters were filled and pressurized with a Teflon membrane pump. Canister sampling is only suitable for small compounds. Concentrations of compounds in the range of C_8-C_{12} were found to be more stable in Tenax adsorbent than in canisters (*Zielinska et al.*, 1996). These compounds are possibly adsorbed onto the canister inner surfaces.

Larger gas-phase organic compounds were collected on adsorbents Tenax-TA and Carbopack-B using pumped sampling. Tenax-TA and Carbopack-B were chosen because they are hydrophobic, thus eliminating the need for sample drying. In the measurements made in 1996-1998 and used for the papers I and III, only Tenax-TA was used. Tenax-TA is a good adsorbent for monoterpenes and sesquiterpenes, but it is not strong enough for isoprene (*Cao & Hewitt*, 1999). Isoprene was analyzed then from canister samples. In the emission rate measurements carried out in 2000, and used for paper III, a mixture of Tenax-TA/Carbopack-B was used, because Carbopack-B is also strong enough for isoprene. Tenax-TA can also be used for more polar compounds (*Köning et al.,* 1995).

The accuracy of the repeated Tenax calibration sample analysis was estimated to be about 6 % for each terpene compound except limonene and 5 % for light hydrocarbon analysis. Limonene was frequently found in blank tubes and therefore analytical error is bigger. In the measurements carried out in 2000, the limonene blank value had decreased to the same level with other monoterpenes.

Constant-flow type pumps were used (Alpha-2, Ametek). Constant-flow pumps can compensate for moderate flow resistance variations between the adsorbent tubes used. Prior to each growing season, all the tubes were checked for their flow restriction. The pumps were calibrated each day before and after the measurements were conducted. The flow rates used were about 100 ml/min. The maximum deviation of flow rates within one day was 10%.

Canister samples were analyzed using a gas chromatograph equipped with flame ionization detector (FID) and Al_2O_3/KCl PLOT column (50 m, i.d. 0.32 mm). Prior to analysis samples were passed through a stainless steel tube (10cm* 1/4’’) filled with K_2CO_3 and NaOH in order to dry them. Water in whole air samples can cause problems by blocking capillaries, varying retention times and shifting the baseline; and water therefore has to be removed from the sample prior to analysis. Air samples were concentrated in two liquid nitrogen traps. The first trap was a stainless steel loop (1/8’’*125cm) filled with glass beads while the other one was a capillary trap. Calibration was performed using a gas-phase standard from NPL (National Physical Laboratory, UK) including 30 hydrocarbons at concentration levels of 1-10 ppb.

Adsorbent tubes were analyzed using a thermodesorption instrument (Perkin-Elmer ATD-400) connected to a gas chromatograph (HP 5890) with HP-1 column (60 m, i.d 0.25 mm) and a mass-selective detector (HP 5972). Samples were concentrated in the thermodesorption instrument in a cold trap (-30°C) filled with Tenax-TA (papers I and III) or a carbon trap (paper II). No sample drying was needed due to the hydrophobic adsorbents. Samples were analyzed using selected ion mode (SIM). Every day one larger volume sample (3-4 litres) was analyzed using full scan mode in order to identify the compounds. The analytical system did not allow the separation of myrcene and β-pinene; their amount was therefore expressed as a sum and quantified as β-pinene. Five-point calibration was utilized using liquid standards in methanol solutions. Standard solutions were injected onto adsorbent tubes that were flushed with helium flow (100ml/min) for five minutes in order to remove methanol. Standards were available for most of the compounds identified; pure ocimene, *cis*-caryophyllene and α-farnesene standards were not accessible and therefore ocimenes were quantified as α-pinene and *cis*-caryophyllene and α-farnesene as *trans*-caryophyllene.

4.3. Emission rate measurements

Several techniques have been utilized to measure the emission fluxes from vegetation. These comprise enclosure, tracer dilution, and micrometeorological methods. The enclosure technique is a plant-specific technique using a plant or a part of it, which is enclosed in a cuvette, whereas the other techniques are used to measure VOC fluxes from a certain land area. In Finland, the gradient method has been used to measure VOC fluxes from pine forests (*Rinne et al.*, 1999, 2000 a, b).

In the present work, the enclosure technique was employed, because plant specific emission rates are needed for emission inventories and so far there were no emission rates available for boreal deciduous trees. A branch of a tree is enclosed in a cuvette made of transparent, inert Teflon. The cuvette is equipped with inlet and outlet ports, a temperature and humidity sensor, a PPFD sensor and a Teflon fan. Air is pumped through the cuvette at a known flow rate. The samples are then collected simultaneously onto adsorbent tubes from both inlet and outlet ports. The emission rate (E) is determined as the mass of compound per leaf or needle dry weight (m) and time according to equation (5).

$$E = (C_2 - C_1) * F * m^{-1} \quad \text{(eq. 5)}$$

C_2 is the concentration in the outgoing air, C_1 is the concentration in the air entering, and F is the flow rate into the cuvette. The dry weight of the biomass was determined by drying the leaves at 75ºC until achievement of weight consistency.

Most of the compounds of interest are very reactive towards ozone, and therefore ozone has to be removed from the incoming air. *Hoffmann et al.* (1995) and *Calogirou et al.* (1996) have measured high losses for some of the reactive terpenes; ocimenes and limonene in particular were found to be destroyed almost completely. MnO_2-coated copper meshes have been found to destroy ozone efficiently and these were used in papers II and III, but in paper I (measurements in 1996) no ozone scrubbers were employed. In our measurement setup in 1996, samples were taken from the outlet port and the ambient air next to the inlet tube situated close to the ground. Although no ozone scrubber was used in 1996, the average standard monoterpene emission potential (30°, according *Guenther et al.*, 1991) of *Betula pendula* during the high emission season was 6.2±4.6 $\mu g\ g^{-1}_{dw}\ h^{-1}$ whereas in 1997, when the ozone scrubber was used, the emission potential was 7.7±4.6 $\mu g\ g^{-1}_{dw}\ h^{-1}$.

Because these emission potentials are so similar, it is likely that most of the ozone was already destroyed by the vegetation close to the ground.

4.4. Monoterpene oxidation reactions in chamber experiments

Papers IV and V present laboratory studies conducted in a laboratory of the Statewide Air Pollution Research Laboratory in the University of California in order to identify the main products formed in atmospheric reactions of monoterpenes with $OH^{\cdot}$ and ozone. The reactions were carried out in a 6400-litre Teflon chamber equipped with black lamps and a Teflon fan. Most of the anticipated products are not commercially available and therefore most of the earlier identifications have been tentative, based on mass spectra alone (*Arey et al.*, 1990). The purpose of the study was to produce enough oxidation products so as to be able to isolate and purify the main products for complete spectroscopic identification. The choice of reaction ($OH^{\cdot}$ radical or O_3) was made on the basis of earlier quantitative yield data for the reactions. The reaction that generated more major products was chosen. Quantitative reactions were carried out using a monoterpene concentration about ten times smaller than that in the reactions used for identification. Reactions were followed with GC/FID and when enough products were formed a 4000-litre gas sample was collected onto 6-8 polyurethane foam plugs with high volume sampler. The plugs were extracted with dichloromethane and concentrated to 2-ml. The oxidation products from these solutions were then separated using a liquid chromatoraph with a diode-array detector as described in paper IV. The solvents used were water/methanol mixtures. For NMR (Nuclear Magnetic Resonance) spectra analysis the solvent needed to be changed to $CDCl_{3.}$ This was done using solid-phase extraction (SPE) on octadecyl columns as explained in paper IV. In addition to NMR analysis, infrared (IR) spectra were also obtained using an FTIR (Fourier transform infrared) detector interfaced to a gas chromatograph.

5. RESULTS

5.1. VOC emission rates

5.1.1. Seasonal variation of VOC emissions

5.1.1.1 Isoprene emitters (*Populus tremula* and *Salix phylicifolia*)

Two of the tree species studied, *Populus tremula* and *Salix phylicifolia,* were isoprene emitters (paper I). The isoprene emissions began about two weeks after the leaves had emerged. On the first measurement day, *Populus tremula* did not emit isoprene, but two weeks later, when *Populus tremula* was measured for the second time, the isoprene emission rate was 45 $\mu g\ g^{-1}{}_{dw}\ h^{-1}$. Also *Salix phylicifolia* did not emit isoprene at two first measurement days in May, but the emissions initiated in June. In August, when the weather was warm, with the temperature exceeding 20°C on every measuring day, the isoprene emission rates of *Salix phylicifolia* were very high (approximately 50 $\mu g\ g^{-1}{}_{dw}\ h^{-1}$). The delayed isoprene emission has been detected also earlier. *Guenther et al*. (1991) noticed that the isoprene emission of eucalyptus leaves increased considerably when the leaves had reached the age of two weeks and *Grinspoon et al*. (1991) found that isoprene emission from velvet bean leaves occurs several days after the photosynthetic competence develops.

Populus tremula and *Salix phylicifolia* emitted monoterpenes soon after bud break, but these emissions declined quite soon, suggesting that the terpenes could be from a pool in the buds. Higher terpene emissions from young leaves can be related to chemical defence mechanisms. Young leaves are sensitive to attacks by insects and herbivores. These emission rates per dry weight (g_{dw}) were, however, significant, the averages of the first measurements at the end of May being 7.9 μg g_{dw}^{-1} h^{-1} and 9.5 μg g_{dw}^{-1} h^{-1} for *Populus tremula* and *Salix phylicifolia*, respectively. *Populus tremula* emitted mainly Δ^3-carene and α-pinene and *Salix phylicifolia* α-pinene, β-pinene, limonene and *trans*-ocimene.

5.1.1.2. Monoterpene emitters (*Betula pendula* and *Betula pubescens*)

Betula pendula and *Betula pubescens* were found to be monoterpene emitters. High monoterpene emission rates were detected soon after bud burst similarly to *Populus tremula* and *Salix phylicifolia*. These early emissions from the *Betula* species are also likely to be residuals from the monoterpene pool in the buds. The buds of birches contain 4%-6% of volatile oils, whereas their leaves contain only 0.05-0.1 % (*Lievonen*, 1982). The monoterpene emission rates were low during the period of leaf growth. Higher monoterpene emission rates were initiated after the leaves had reached their full size and were darker and harder. As discussed in the previous chapter, the isoprene emission from *Populus tremula* and *Salix phylicifolia* initiated about two weeks after budburst, but a longer time was needed for the commencement of monoterpene emission from the *Betula* species. According to the statistics of the Finnish Forest Research Institute, the onset of leafing of *Betula pubescens* took place during the period June 1- June 11 in 1997 and from May 10 to May 25 in 2000 at the measurement site at the Ruotsinkylä Research Station. The first high monoterpene emission rates were measured in 1997 on June 30 and in 2000 on June 22. The time needed for monoterpene emission induction would thus appear to be 3-5 weeks. Such statistics were not available for *Betula pendula*.

At the time of induction the monoterpene emission pattern also changed (Table 2 and 3). In early summer the monoterpenes consisted of α-pinene, β-pinene, Δ^3-carene and sabinene, whereas later in summer the emission consisted mainly of ocimenes and sabinene. The ocimene and sabinene emissions declined at the end of September, as the growing season was ending.

The VOC emissions of *Betula pendula* and *Betula pubescens* showed also differences. *Betula pubescens* emitted sesquiterpenes and linalool in addition to monoterpenes. These emissions were strongest early summer and they declined earlier than the monoterpene emissions (Fig. 1, paper II). The emissions of *Betula pubescens* had also large tree-to-tree variations; not all trees measured in 1997 initiated higher monoterpene emission rates (Table 3). To test if these differences were tree-to-tree or day-to-day variations, two different *Betula pubescens* clones were measured during the growing season in 2000. After the leaves were fully-grown and dark green, one clone (E567) initiated high monoterpene emission rates, whereas the other (D2472) did not. The monoterpene emission rates of D2472 actually decreased a little. The emissions of the two clones also differed qualitatively. Both emitted terpinolene in early summer, but later clone E567 changed to emit mainly sabinene (Table 4), whereas clone D2472 changed to emit mainly *trans*-ocimene, in addition to terpinolene during the late summer (Table 5). Both clones emitted linalool in June, whereas later in summer linalool emissions were rare. Sesquiterpene (*trans*-

caryophyllene) emission rates were also higher early in the summer, their emissions starting earlier and also decreasing earlier than the monoterpene emissions. The young trees measured in 1997 emitted less sesquiterpenes than the adult clones, but those young trees that emitted monoterpenes emitted more than the clone E567, which had higher emission rates. It is possible that the age of the trees explains some of the observed variability, but the reason for large tree-to-tree variations in the monoterpene emission rates is likely to be due to the different genetic origins.

Table 2: Relative amount of terpenoids (% of total) in the emissions of *Betula pendula*, during the growing season of 1997. The values are averages of 2-4 daily measurements. The two last lines show the total emission rate in μg g_{dw}^{-1} h^{-1} and the emission potential standardized to 30°C according to *Guenther et al.*, (1991).

	May 22	May 26	May 28	Jun 2	Jun 3	Jun 10	Jun 17	Jun 25	Jul 1	Aug 18	Aug 21	Aug 22	Sep 3	Sep 8	Sep 18	Sep 24
α-pinene	15	22	61	6	54	7	9	15	12	3	1	1	9	13	16	12
Camphene	6	3	14	0	4	0	1	0	0	0	0	0	1	0	0	0
Sabinene	55	50	2	38	3	3	2	75	61	2	0	3	59	75	32	7
β-pinene	15	8	13	51	20	18	5	7	6	2	1	3	18	4	22	35
Δ^3-carene	9	3	9	3	10	3	4	0	0	0	0	5	1	0	3	2
Cis-ocimene	0	0	0	1	0	11	26	0	6	33	34	23	1	0	0	4
Limonene	0	13	0	1	9	18	0	2	2	1	1	4	10	7	0	40
Trans-ocimene	0	0	0	0	0	40	52	1	12	59	63	61	1	0	27	1
Total emission rate	0.83	0.11	0.16	1.03	0.08	0.78	0.53	2.33	12.4	6.18	6.14	1.34	3.67	6.32	0.06	0.53
Monoterpenes (30°C)	3.5	0.41	0.37	1.6	0.19	0.96	0.90	5.7	9.1		5.8	1.5	8.3	15.9	0.44	3.0

Table 3: Relative amount of terpenoids (% of total) in the emissions of *Betula pubescens*, during the growing season of 1997. The values are averages of 2-4 daily measurements. The four last lines show the total emission rate in μg g_{dw}^{-1} h^{-1} and the total emission potential (standardized to 30°C according to *Guenther et al.*, (1991)) of monoterpenes (linalool not included), linalool and sesquiterpenes. The β-coefficients used in the standardization were 0.09°C^{-1}, 0.18 °C^{-1}, and 0.19°C^{-1} for monoterpenes, linalool, and sesquiterpenes, respectively.

	May 22	May 28	Jun 2	Jun 5	Jun 10	Jun 11	Jun 13	Jun 18	Jun 25	Jun 30	July 1	Aug 21	Aug 22	Sep 8	Sep 18	Sep 29
α-Pinene	35	33	19	17	0	5	7	5	7	10	1	27	10	17	20	0
Camphene	2	20	4	1	0	0	1	1	2	0	0	8	0	7	4	0
Sabinene	17	3	15	2	0	12	23	1	2	78	0	15	81	8	16	29
β-Pinene	17	7	10	10	1	9	8	3	7	7	2	11	6	4	16	2
Δ^3-Carene	0	5	4	6	0	5	3	4	6	0	1	15	0	0	8	2
cis-Ocimene	0	0	0	0	0	3	2	0	0	0	0	0	0	15	0	0
Limonene	17	4	2	1	1	9	0	17	16	1	2	20	1	10	29	44
1,8-cineol	4	14	3	0	0	4	2	1	3	1	0	1	1	0	4	0
trans-Ocimene	0	0	0	0	2	6	12	4	5	1	1	4	0	28	2	22
Linalool	9	13	2	50	93	46	41	42	25	1	48	0	1	0	0	0
trans-Caryophyllene	0	0	41	13	1	0	0	21	27	0	26	0	0	0	0	0
cis-Caryophyllene	0	0	0	0	0	0	0	0	0	0	13	0	0	0	0	0
α-Farnesene	0	0	0	0	0	0	0	0	0	0	6	0	0	11	0	0
Total emission rate	0.46	0.21	1.19	0.76	11.2	1.17	1.32	0.49	0.73	12.7	8.90	0.13	18.0	0.15	0.27	0.08
Monoterpenes (30°C)	1.5	0.55	0.92	0.55	0.70	0.93	0.92	0.45	0.87	13.6	0.38	0.23	26.2	0.34	2.0	0.31
Linalool (30°C)	0.62	0.23	0.05	1.5	12.7	1.1	0.75	1.5	1.0	0.20	1.3	0	0.30	0	0	0
Sesquiterpenes (30°C)	0	0	0.92	0.42	0.16	0	0	0.76	1.07	0	1.2	0	0.11	0.12	0.09	0

Table 4: Relative amount of terpenoids (% of total) in the emissions of *Betula pubescens*, clone E567, during the growing season of 2000. The values are averages of 2-6 daily measurements. The four last lines show the total emission rate in μg g_{dw}^{-1} h^{-1} and the total emission potential (standardized to 30°C according to *Guenther et al.*, (1991)) of monoterpenes (linalool not included), linalool and sesquiterpenes. The β-coefficients used in the standardization were 0.09°C^{-1}, 0.18 °C^{-1}, and 0.19°C^{-1} for monoterpenes, linalool, and sesquiterpenes, respectively.

	June 9	June 13	June 15	June 21	June 22	June 29	July 4	July 7	July 11	July 14	July 18	July 27	Aug 1	Aug 8	Aug 11	Aug 22	Aug 25	Aug 28	Aug 30
α-pinene	0	0	1	0	1	1	2	5	4	3	4	5	6	4	8	3	5	0	0
Camphene	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	2
Sabinene	0	1	5	1	6	6	21	64	40	36	35	65	68	54	57	26	37	6	47
β-pinene	0	0	0	0	0	0	1	3	2	2	2	4	4	3	2	2	4	0	0
Δ^3-carene	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6	0	1	0	10
Ocimene	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
Limonene	0	0	0	0	0	0	1	1	1	0	1	1	1	0	3	1	1	0	5
1,8-cineol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
trans-ocimene	0	0	0	0	1	0	1	1	1	2	1	1	1	3	6	13	2	1	6
Terpinolene	9	5	11	1	11	0	1	1	1	1	1	1	1	1	1	1	0	0	0
Linalool	16	13	21	2	18	2	8	1	1	2	1	0	0	0	1	0	0	1	0
Trans-caryophyllene	75	80	62	95	63	90	65	23	51	53	56	23	18	35	16	55	49	91	30
Total emission rate	2.49	0.92	0.50	12.5	9.78	10.7	2.04	4.45	2.09	0.79	3.74	0.92	0.70	0.44	0.59	2.01	4.60	10.3	0.52
Monoterpenes (30°C)	0.53	0.14	0.25	0.54	2.4	1.7	1.2	6.6	2.2	1.2	3.1	1.7	1.7	0.82	1.5	1.3	3.0	1.0	0.67
Linalool (30°C)	2.2	0.55	0.88	0.63	3.1	0.55	0.73	0.16	0.08	0.24	0.13	0	0	0	0.08	0	0	0.12	0
Sesquiterpenes (30°C)	11.5	3.6	3.0	27.2	10.9	35.1	6.5	4.2	5.7	6.1	8.4	1.4	1.2	1.4	1.0	1.9	3.1	11.1	0.48

Table 5: Relative amount of terpenoids (% of total) in the emissions of *Betula pubescens*, clone D2472, during the growing season of 2000. The values are averages of 2-4 daily measurements. The four last lines show the total emission rate in μg g_{dw}^{-1} h^{-1} and the total emission potential (standardized to 30°C according to *Guenther et al*., (1991)) of monoterpenes (linalool not included), linalool and sesquiterpenes. The β-coefficients used in the standardization were 0.09°C^{-1}, 0.18 °C^{-1}, and 0.19°C^{-1} for monoterpenes, linalool, and sesquiterpenes, respectively.

	Jun 9	Jun 13	Jun 15	Jun 21	Jun 22	Jun 27	Jun 29	July 4	July 6	July 11	July 14	July 18	July 27	Aug 1	Aug 28
α-pinene	1	0	1	0	1	6	5	3	0	0	0	0	1	0	0
Camphene	1	0	0	0	0	1	0	0	0	0	2	0	0	0	0
Sabinene	0	2	0	0	1	2	2	0	0	0	4	0	1	0	0
β-pinene	0	0	0	0	1	8	8	1	0	0	12	0	3	0	3
Δ^3-carene	0	0	1	0	0	1	0	2	0	0	12	0	0	0	0
Cis-ocimene	0	0	0	0	0	1	4	0	0	1	0	0	1	1	4
limonene	1	0	1	0	1	1	0	1	0	0	7	1	0	0	0
1,8-cineol	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0
trans-ocimene	0	0	1	1	1	2	2	12	10	12	54	22	27	48	57
terpinolene	12	27	14	7	15	0	1	1	0	7	9	1	1	1	0
linalool	29	50	29	14	25	11	9	10	41	0	0	7	23	11	0
Trans-caryophyllene	55	20	52	76	53	67	70	71	48	80	0	68	44	39	36
Total emission rate	0.25	1.20	0.38	0.43	3.21	0.44	1.18	0.17	0.91	0.30	0.02	0.12	0.27	0.08	0.13
Monoterpenes (30°C)	0.09	0.68	0.17	0.05	0.52	0.23	0.50	0.05	0.09	0.09	0.06	0.05	0.16	0.10	0.10
Linalool (30°C)	0.39	2.1	0.64	0.08	0.44	0.29	0.41	0.05	0.25	0	0	0.02	0.20	0.05	0
Sesquiterpenes (30°C)	0.80	0.86	1.3	0.47	0.90	1.9	3.6	0.35	0.29	0.59	0	0.22	0.41	0.19	0.11

5.1.1.3. Use of effective temperature sum (ETS) to describe the seasonality of the emission rates

The seasonal variations of the emission rates are described in terms of the effective temperature sum. The Effective Temperature Sum (ETS) (calculated as the accumulated daily average temperature sum above a threshold temperature, usually 0 or 5 °C, and expressed in degree days (d.d.)) has been widely used to estimate the time of onset of the leafing and flowering of plants (*Hari & Häkkinen* 1991; *Lappalainen* 1993). *Monson et al.* (1994) applied ETS to predict the springtime induction of isoprene emission from aspen in different environments. According to the statistics of the Finnish Forest Research Institute, the use of ETS instead of calendar dates reduces variability between different years. The leaves of *B. pubescens* at the Ruotsinkylä Research Station emerged during the period 20 May-1 June in 1997 (corresponding to an ETS of 75-126 d.d.) and 7 May-10 May in 2000 (ETS 99-125 d.d.). The onset of leafing took place between 1 June-11 June in 1997 (ETS 126-239 d.d.) and 10 May-29 May in 2000 (ETS 125-250 d.d.). Although the leaves were fully grown almost two weeks earlier in 1997 than in 2000, the effective temperature sums are quite similar. In 1997 and 2000, 400 d.d. were reached on 25 June and 18 June, respectively. High monoterpene (especially sabinene) emission rates were also measured a week earlier in 2000 than in 1997 (30 June 1997 and 22 June 2000), although the poor data coverage and large tree-to-tree variations within *Betula pubescens* trees in 1997 do not allow one to make firm conclusions about the date of the initiation of higher monoterpene emission rates.

In 1997 ambient monoterpene concentrations were measured at Ilomantsi (paper III) and the emission rates of *Betula* species at Ruotsinkylä (paper II), while in 1996 isoprene concentrations were measured at Ilomantsi and the emission rates of the isoprene emitters *Populus tremula* and *Salix phylicifolia* at Ruotsinkylä. On the basis of this limited data, the use of ETS would also appear to reduce the emission rate variability between different locations. The forest surrounding the measuring site at Ilomantsi is composed of *Pinus sylvestris, Picea abies*, *Populus tremula* and *Betula pendula* with few *Betula pubescens* trees and *Salix* species. The *Pinus sylvestris* of the area emit only minor amounts of sabinene (*Rinne et al*., 1999), and *Populus tremula* does not emit it at all (paper I), so the sabinene concentrations are likely to be from the *Betula* species. Aspens are the most important source for isoprene at this site. To test if ETS would be more accurate than calendar dates to be used in emission inventories, the emission rates measured in Ruotsinkylä are plotted together with the ambient concentrations measured in different location, at Ilomantsi (about 400 km apart) in Fig. 2. Figure 2 shows the dates on which the isoprene/sabinene emission rates were high for the first time together with the dates of previous measurements and the corresponding degree days. Compared to the calendar dates the degree days fit better with the measured ambient concentrations at Ilomantsi. More frequent emission rate measurements would be needed to find out the induction of the emissions accurately. Linalool and sesquiterpenes also show seasonal variability, with higher emission rates measured in June. However, these compounds are too reactive to be found in the ambient air samples. Table 6 shows the mean emission potentials for the *Betula* species measured.

Table 6. The emission potentials of *B. pendula* and *B. pubescens* (average and standard deviation, $\mu g\ g_{dw}^{-1}\ h^{-1}$) for different seasons. For *B. pubescens*, the data set from 1997 and the two clones measured in 2000 are shown separately due to large variations. The β-coefficients used in the standardization were $0.09^{\circ}C^{-1}$, $0.18\ ^{\circ}C^{-1}$, and $0.19^{\circ}C^{-1}$ for monoterpenes, linalool, and sesquiterpenes, respectively. The number of observations is in the parentheses.

	B. pendula, 1997	*B. pubescens*, 1997	*B. pubescens*, 2000, E567	*B. pubescens*, 2000, D2472
monoterpenes				
ETS<80	3.63 ± 0.38 (2)	1.47 ± 0.14 (2)	no data	no data
80<ETS<400	0.68 ± 0.57 (14)	0.72 ± 0.24 (18)	0.31 ± 0.21 (6)	0.31 ± 0.43 (6)
ETS>400	7.71 ± 4.64 (12)	5.49 ± 9.22 (16)	1.71 ± 1.40 (46)	0.17 ± 0.18 (23)
linalool				
ETS<600	-	1.79 ± 3.27 (26)	1.20 ± 0.99 (15)	0.67 ± 0.89 (15)
ETS>600	-	0.06 ± 0.13 (10)	0.08 ± 0.17 (37)	0.07 ± 0.10 (14)
sesquiterpenes				
	-	0.31 ± 0.53 (36)	6.94 ± 10.85 (52)	0.81 ± 0.95 (29)

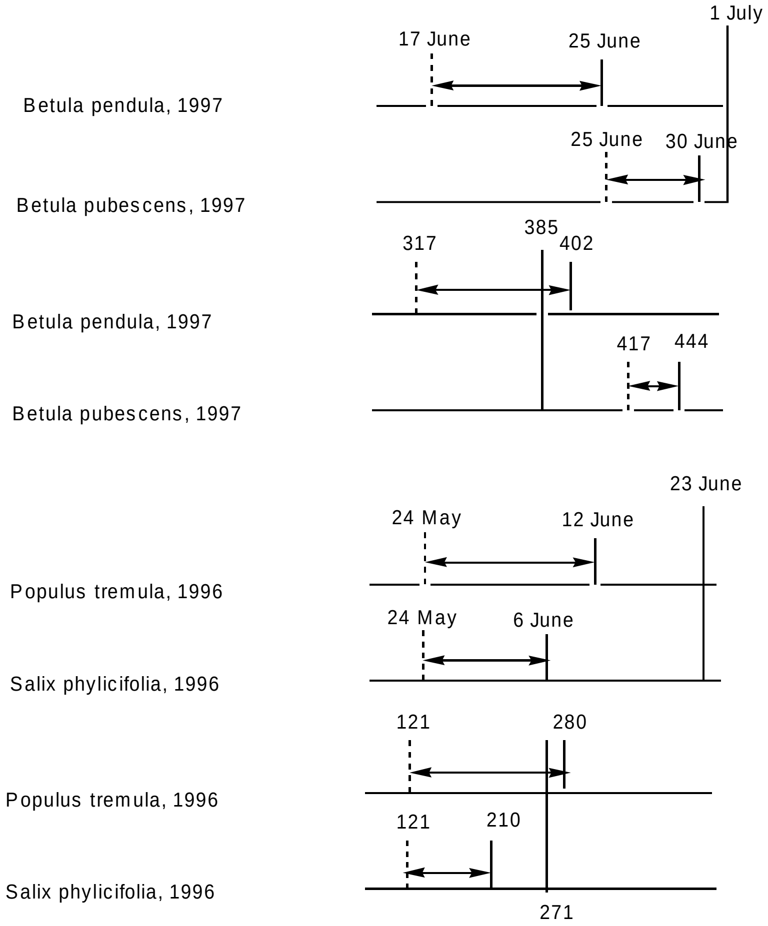


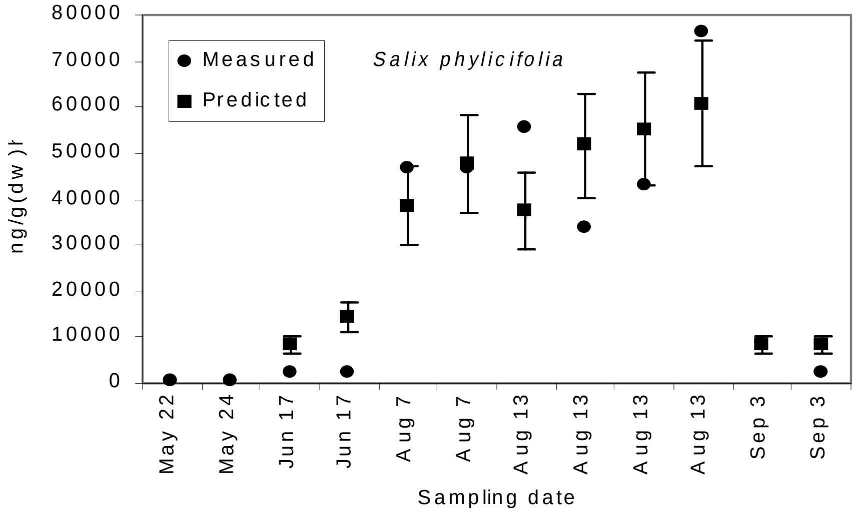
Figure 2: Short, solid vertical lines represent the days on which, at Ruotsinkylä, higher monoterpene emission rates were measured for the first time for *Betula* species and higher isoprene emission rates for *Salix phylicifolia* and *Populus tremula*. Short dotted lines represent the dates when the previous measurements were conducted. Below the graphs presenting the observations using calendar dates are shown the corresponding ETS values at Ruotsinkylä. The long vertical line shows when sabinene (for *Betula* species) and isoprene (for *Salix phylicifolia* and *Populus tremula)* concentrations increased at Ilomantsi with the corresponding ETS value there.

5.1.2. VOC emission rate dependence on physical factors

The isoprene emission rates were correlated with both temperature and photosynthetic photon flux density (PPFD), although our measurements were conducted on different days, around midday, thus not reflecting the diurnal variation. The standard isoprene emission potentials (at T=30°C and PPFD=1000 μmol s^{-1} m^{-2}), 43 μg g_{dw}^{-1} h^{-1} and 39 μg g_{dw}^{-1} h^{-1} for *Populus tremula* and *Salix phylicifolia*, respectively, were determined by applying non-linear regression analysis between emission and temperature and light (equations 1, 2 and 3). Figure 3 shows the measurements together with the model results. The data prior to isoprene emission induction was excluded. The correlation coefficients for model results and measured emission rates are $r^2=0.84$ and $r^2=0.76$ for *Populus tremula* and *Salix phylicifolia*, respectively.

We did not find any clear dependence on PPFD for emission rates either for the sum of terpenes or for any individual terpenoid compound for any of the tree species studied. However, when one branch of clone E567 was covered and samples were collected from the dark cuvette, emissions of almost all the monoterpenes decreased, whereas sesquiterpene emission rates were not much affected (paper II). Linalool emission rates also decreased but not as much as those of monoterpenes. After the cuvette was exposed to light again, the emission rates started to increase. One reason for the poor correlation between PPFD and emission rates may be that trees do not respond to changes in light intensity immediately, but that rather there is a delay during which trees adjust themselves to the new conditions. In the darkening experiment, the emission rates did not recover to their initial values within 30 minutes, but remained clearly lower at about half of the initial value. The monoterpene, linalool and sesquiterpene emission rates from *Betula* species are dependent on temperature (paper II, Table 2), although the correlations are rather poor.

Rough handling of *Betula pubescens* caused high 3-hexenylacetate, 3-hexen-1-ol, 1-hexanol and 2-hexenal emission rates, but did not affect the monoterpene emissions (paper II, Table 3). The high emission rates did not last long: the samples taken one hour later were already close to the normal values.



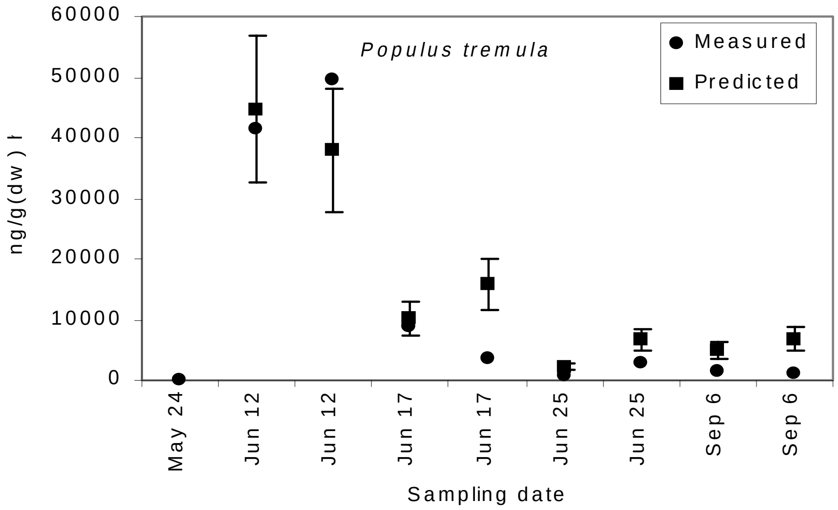


Figure 3: Isoprene emission rate data (Ruotsinkylä, 1996) fitted to the isoprene emission model by Guenther et al. (1991, 1993,1997).

5.2. Concentrations of isoprene and monoterpenes in ambient air

The concentrations of α-pinene, β-pinene/myrcene, Δ^3-carene, camphene and 1,8-cineol started to increase at Ilomantsi in late May/early June (Fig. 4). The concentrations were highest in June and July, and the correlation between α-pinene, β-pinene/myrcene, and Δ^3-carene was good. The concentrations decreased in August, and in September and in October they were low.

Sabinene concentrations were low until the end of June, increasing about a month later than the concentrations of pinenes, 1,8-cineol and 3-carene. The late sabinene increase is probably from the delayed emission from *Betula pendula.* Ocimenes were also detected from the emission of *Betula pendula*, but these are very reactive towards ozone and the $OH^{\cdot}$ radical (Table 1), and were found only occasionally in the ambient air samples, and then in very low concentrations. Sabinene concentrations were better correlated with isoprene than with other monoterpenes (Fig. 4).

Isoprene concentrations started to increase in the middle of June, 2-3 weeks later than most of the monoterpene concentrations and about a week earlier than sabinene, the maximum appearing concomitant with the sabinene maximum. During August, the concentrations of isoprene and sabinene decreased, earlier than other monoterpenes. Figure 5 shows monthly mean concentrations of different compound groups together with their reactivity-scaled concentrations. Based on OH-reactivities, concentrations were scaled to propylene equivalents according to *Chameides et al.* (1992) (eq. 6).

$$\text{Propy-equiv (j)} = \text{conc. (j.)}\,\frac{k_{OH}(j)}{k_{OH}(C_3H_6)} \qquad \text{(eq. 6)}$$

Because the OH-reactivity-based method accounts for a species' rate of reaction as well as its atmospheric concentration, it provides a more accurate picture than does concentrations alone. Figure 5 shows that although the concentrations of monoterpenes are quite low, much lower than the concentrations of light hydrocarbons, they contribute significantly to the local reactivity of the measured VOCs.

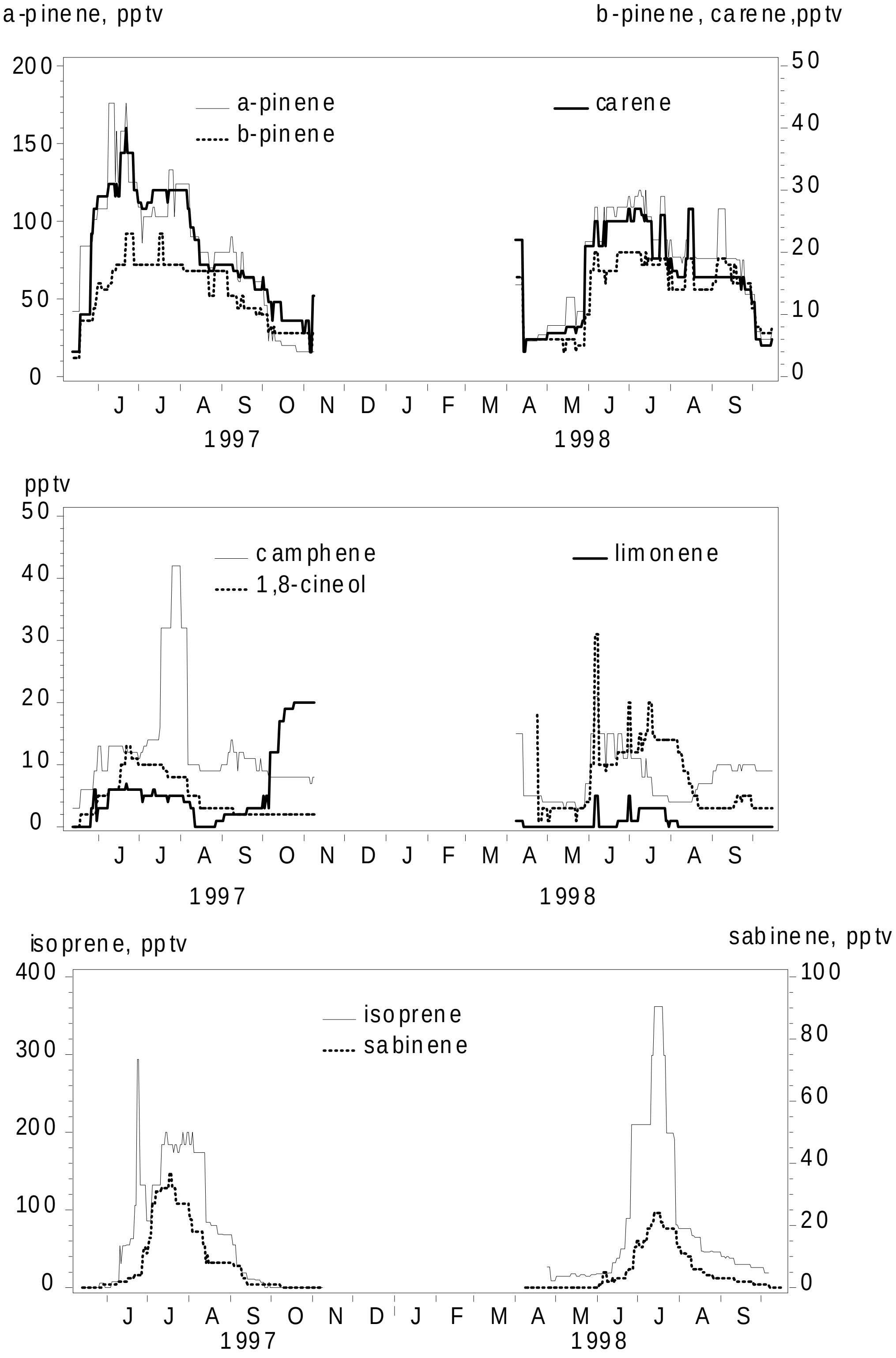


Figure 4: 30-day running median of ambient concentrations at Ilomantsi, Finland.

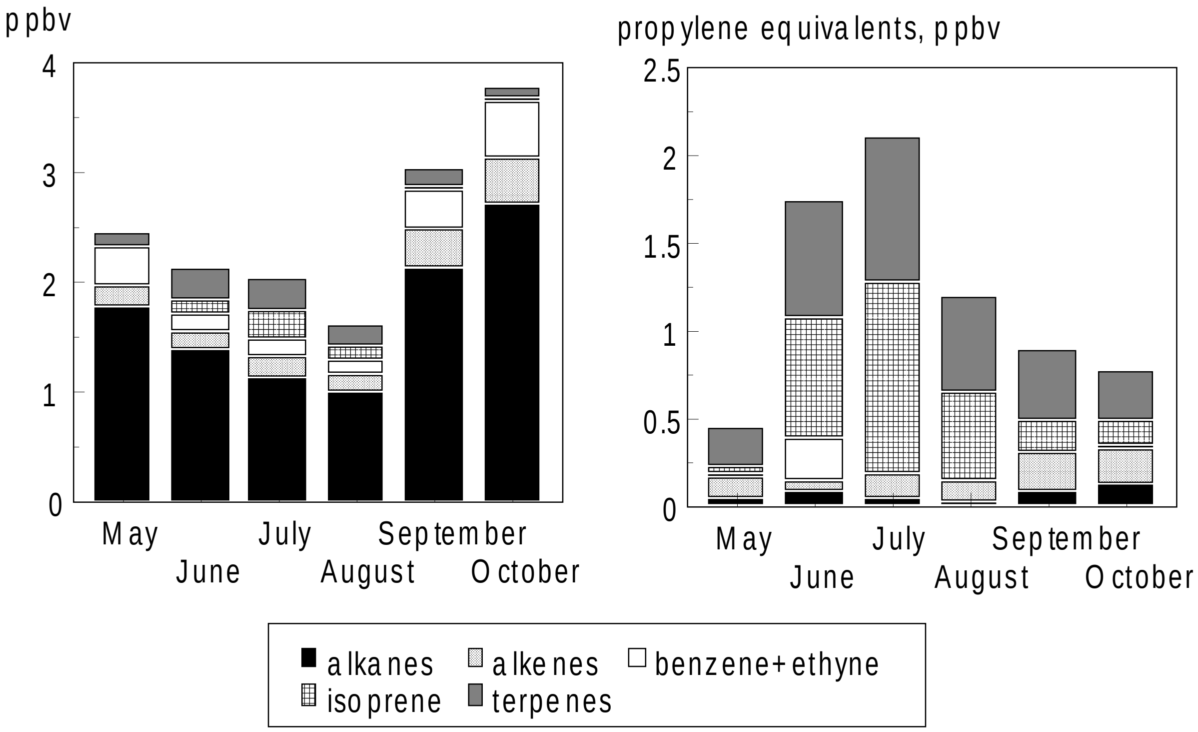
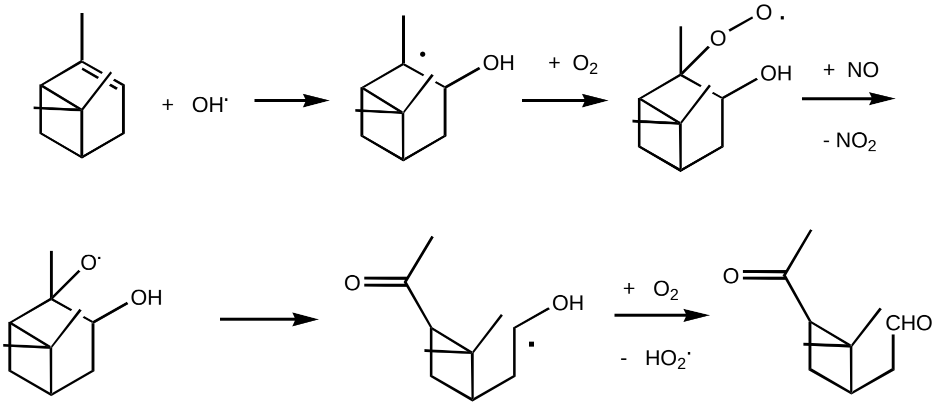


Figure 5: Monthly average concentrations (1997 and 1998) of isoprene, sum of monoterpenes, alkanes (C_2-C_6), alkenes (C_2-C_6, isoprene excluded) and sum of benzene and acetylene together with their OH-reactivity-scaled concentrations (propylene equivalents).

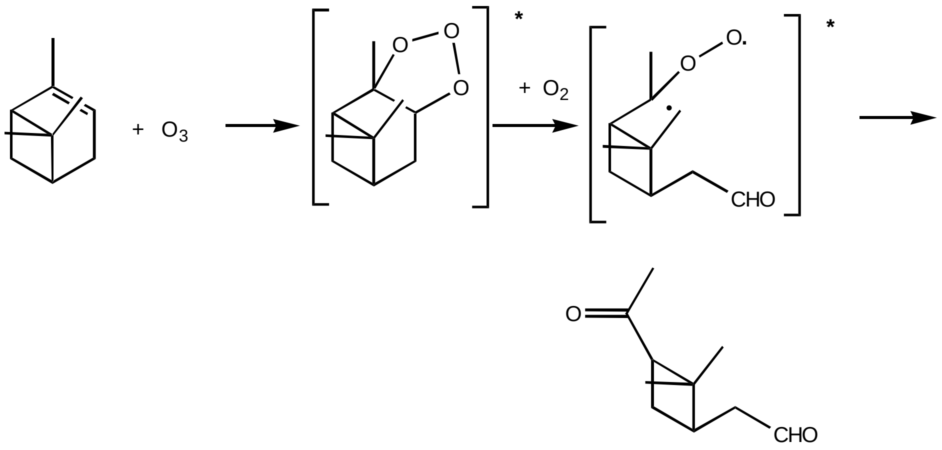
5.3. Products from the reactions of monoterpenes with O_3 and $OH^·$

Samples were collected on PUF plugs from the reaction chamber in order to isolate and purify products formed in the reactions and to conduct spectroscopic identification using MS, gas-phase FTIR and ^{1}H NMR. Commercial standards were available for camphenilone, nopinone and 4-acetyl-1-methylcyclohexene. In general, monoterpenes with double bonds in the ring produced keto-aldehydes and monoterpenes with double bonds external to the ring produced ketones. Limonene, β-phellandrene and terpinolene have two double bonds; one in the ring and the other one external to the ring (Figure 1). The external bond of terpinolene and β-phellandrene was favoured and an addition reaction to it yielded more products. Both double bonds of limonene reacted with hydroxyl radical, but not with ozone. Camphene reacted with the hydroxyl radical only very slowly and the reactions of Δ^3-carene and limonene also yielded only very small amounts of carbonyl products. The products identified and their formation yields are shown in Figure 6. This was the first time when products were identified for the oxidation of terpinolene and Δ^3-carene, and it confirmed other tentative identifications. The OH radical reaction proceeds as described in reactions (8)-(12). The reaction mechanism for α-pinene as an example is:



(30)

The products identified for the ozone reactions are also those expected on the basis of the mechanism presented in reaction 19, except for the lactone. An example of monoterpene reaction with ozone is the oxidation of α-pinene:



(32)

As shown in paper V, carbonyls are produced with 20-30 % formation yield in the OH radical reaction with α-pinene, β-pinene, limonene, Δ^3-carene, β-phellandrene, sabinene and terpinolene, but with only less than 2 % yield in the reaction with camphene. There are only few quantitative yield data available for the monoterpene reactions with the hydroxyl radical. The pinonaldehyde yields for the α-pinene reaction have been reported also by *Arey et al*. (1990) (30 ± 5 %), *Hatakeyama et al*. (1991) (56 ± 4 %), *Vinckier et al*. (1998) (31 ± 15 %) and *Noziere et al*. (1999) (87 ± 29 %). The data by *Arey et al*. and *Vinckier et al*. are in good agreement with the data presented in paper V (28 ± 5 %). *Hatakeyama et al*. (1991) and *Noziere et al*. (1999) used in situ long-path Fourier transform infrared spectroscopy (FTIR) for the quantification whereas the other results have been obtained using gas-chromatographic techniques. Different techniques can cause the observed variations in product yields. FTIR can detect also other carbonyls present in the reaction chamber. β-Pinene reactions have also been studied by *Hatakeyama et al* (1991) using FTIR and again their production yield is higher (79 ± 8 %) than that observed in paper V (27 ± 4 %).

Product yields for the ozone reactions were also less than unity, suggesting that other products are formed as well. *Alvarado et al*. (1998) identified and quantified also other products for the reaction of α-pinene with ozone. Pinonaldehyde was the main product found also in that study and the yield (14 %) was in a reasonable agreement with the yield measured in paper V (19 %).

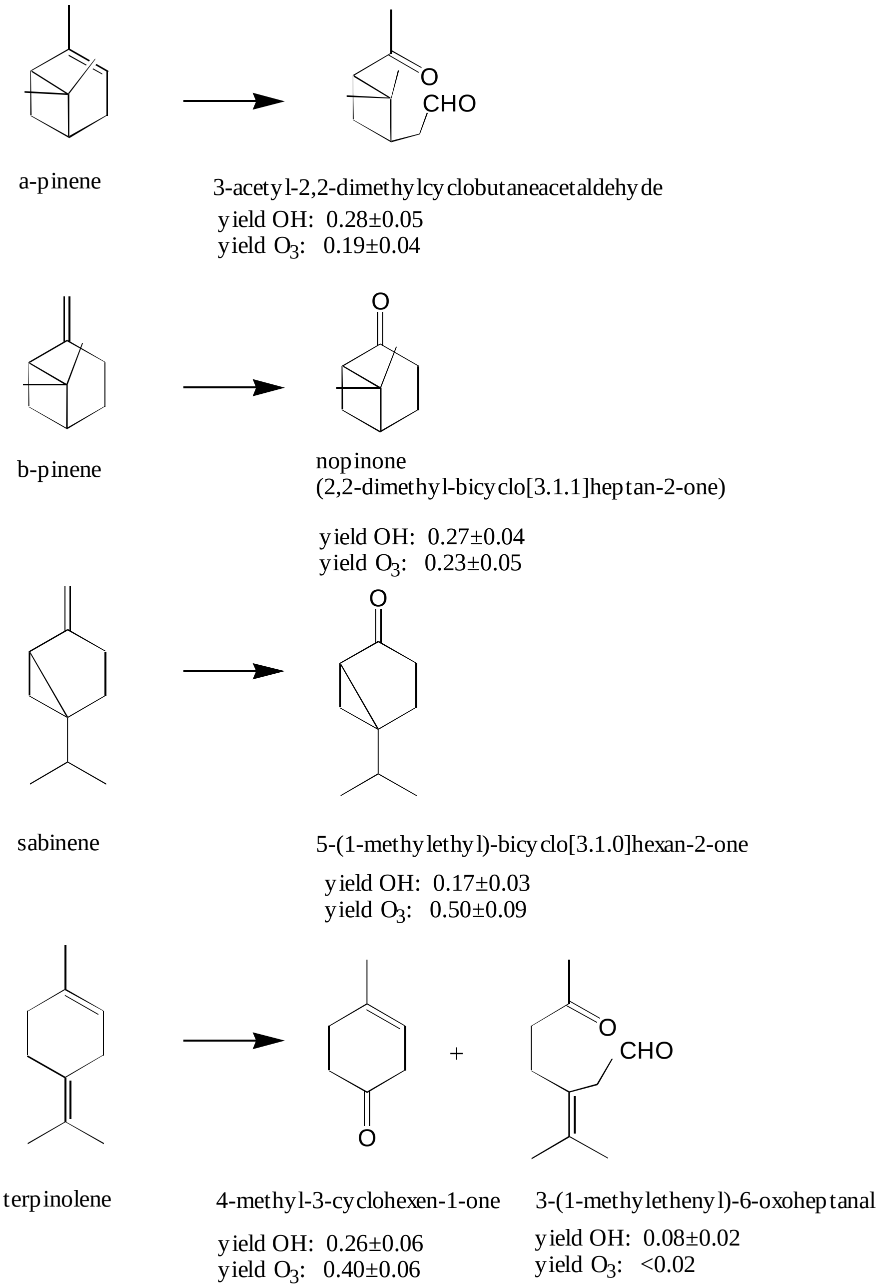


Figure 6a: Carbonyl products, and their formation yields, identified from the reaction of monoterpenes with the OH$^{\cdot}$ radical and ozone.

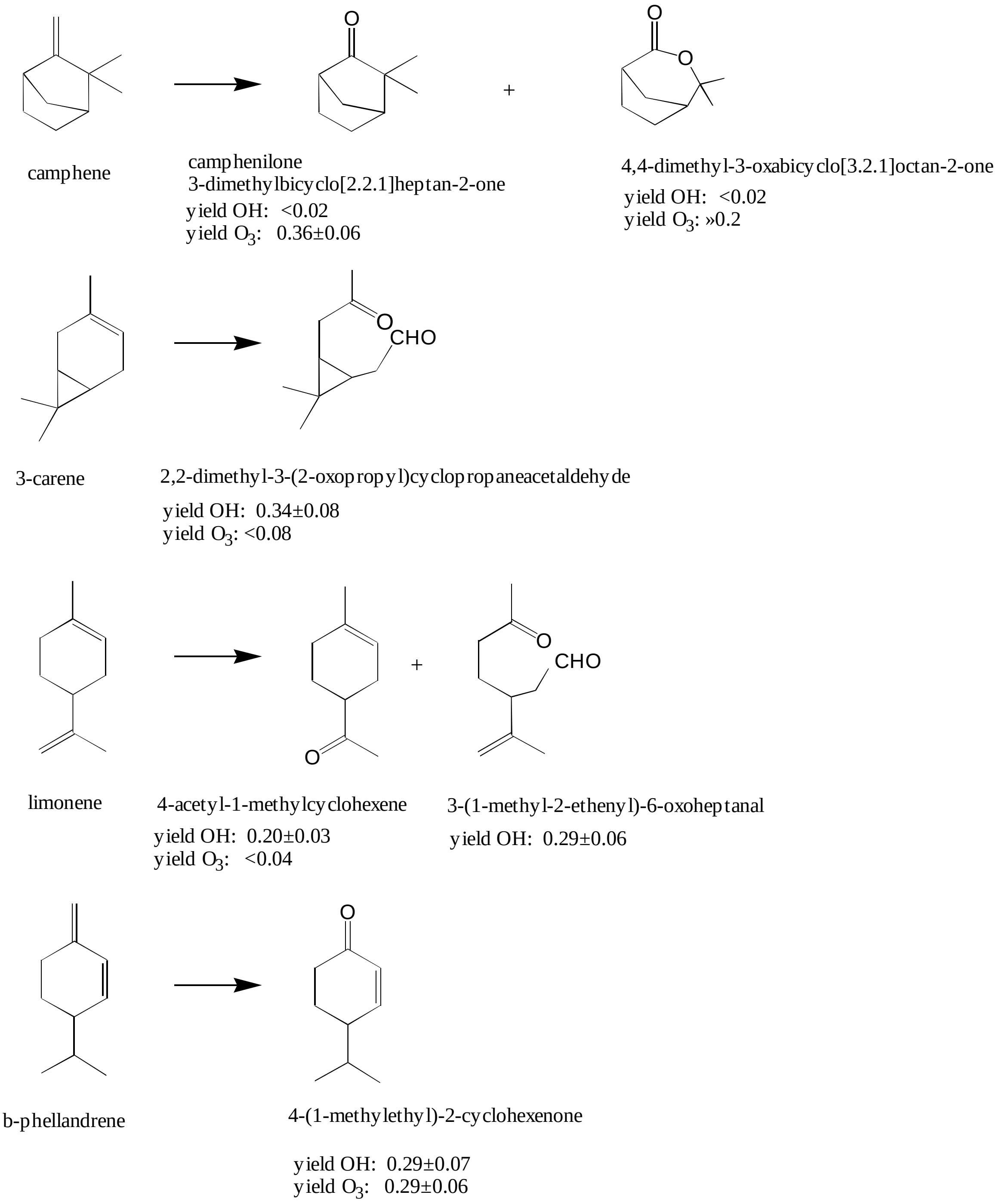


Figure 6b: Carbonyl products, and their formation yields, identified from reaction of monoterpenes with the OH˙ radical and ozone.

Many other products have been reported for the oxidation reactions of monoterpenes, but only few have been quantified. *Calogirou et al.* (1999) have reviewed the gas-phase terpene oxidation products. Some of the carbonyl products identified in papers

IV and V have also been detected in ambient air samples. *Helmig & Arey* (1992) found nopinone (an oxidation product of β-pinene) in forest air in California. Nopinone and pinonaldehyde were also detected above the forest at Hyytiälä in Central Finland (*Spanke et al.*, 2001). The maximum concentrations (pinonaldehyde 140 ppt, nopinone 45 ppt) were observed during the early morning hours.

Carbonyl products are also themselves reactive towards the hydroxyl radical and ozone, and they contribute to tropospheric ozone formation. The oxidation processes of the carbonyls produce many organic acids and di-acids and these compounds can have a very important effect on organic aerosol formation (*Jang & Kamens*, 1999).

6. CONCLUSIONS

The VOC emission rates of the most common boreal deciduous trees were measured. *Populus tremula* and *Salix phylicifolia* were high isoprene emitters with standard emission potentials of 43 $\mu g\ g_{dw}^{-1}\ h^{-1}$ and 39 $\mu g\ g_{dw}^{-1}\ h^{-1}$ for *Populus tremula* and *Salix phylicifolia*, respectively. The *Betula* species emitted monoterpenes and *Betula pubescens* emitted also sesquiterpenes and linalool. These emissions showed seasonal variations and they cannot be expressed with just one emission potential, but the phenology of the tree has to be taken into account (Table 6). Some of the emission potentials have already been used as input data in model estimates of biogenic volatile organic compound emissions from the forests in Finland together with meteorological data and satellite land cover information (*Lindfors & Laurila*, 2000; *Lindfors et al.*, 2000).

In addition to phenological changes, the emission rates were also affected by the age of the tree, its genetic origin, physical disturbance, temperature and light which can cause large uncertainties in the emission calculations. On the basis of this study it is obvious that when determining the emission rates, it is necessary to measure the emissions throughout the growing season. Because of the genetic variability, several trees of the same species should be investigated. Also comparisons with flux measurements would be important in validating the emission rates.

The ambient air concentration measurements can also be used to validate seasonal changes in the emission rates. For example, sabinene concentrations were found to increase later in summer, in agreement with the emission rate measurements. The summer monthly mean concentrations of monoterpenes measured in eastern Finland on a field on top of a hill were 0.16-0.32 ppb. Isoprene concentrations were about as high 0.07-0.35 ppb. Biogenic hydrocarbons contribute significantly to the total reactivity towards the OH radical in rural areas. During the summer months they account for almost all of the measured hydroxyl radical reactivity.

In the oxidation reactions by OH radicals and ozone monoterpenes form carbonyl products. The products were those expected from the addition reaction to the double bond. Camphene also produced a lactone. Product yields were at the most 50%, so most of the products were not accounted for. This was the first definitive identification of the keto-aldehyde product from Δ^3-carene product and the ketone product from terpinolene. Unidentified products can be for example organic acids, hydroxycarbonyls or other multifunctional compounds. New analytical techniques, such as liquid chromatograph connected to a mass-selective detector will help detecting also these compounds.

REFERENCES

Air Quality Measurements 2000: Leinonen L. (ed.), *Finnish Meteorological Institute*.

Alvarado A., Tuazon E.C., Aschmann S.M., Atkinson R. & Arey J., 1998: Products of the gas-phase reactions of O(^{3}P) atoms and O_3 with α-pinene and 1,2-dimethyl-1-cyclohexene. *J. Geophys. Res. 103*, 25541-25551.

*Arey J., Atkinson R. & Aschmann S. M.,*1990: Product study of the gas-phase reactions of monoterpenes with the OH radical in the presence of NO_x. *J. Geophys. Res. 95*, 18539-18546.

Arey J., Winer A. M., Atkinson R., Aschmann S. M., Long W. D., Morrison C. L., & Olszyk D. M., 1991 a: Terpenes emitted from agricultural species found in California’s Central Valley. *J. Geophys. Res. 96,* 9329-9336.

Arey J., Winer A.M., Atkinson R., Aschmann S.M., Long W.D. & Morrison C.L., 1991 b: The emission of (Z)-3-hexen-1-ol, (Z)-3-hexenylacetate and other oxygenated hydrocarbons from agricultural plant species. *Atmos. Environ. 25A,* 1063-1075.

Arey J., Crowley D. E., Crowley M., Resketo M. & Lester J., 1995: Hydrocarbon emissions from natural vegetation in California’s south coast air basin. *Atmos. Environ. 29*, 2977-2988.

Aschmann S.M., Arey J. & Atkinson R., 2000: Formation of β-hydroxycarbonyls from the OH radical initiated reactions of selected alkenes. *Environ. Sci. Technol. 34*, 1702-1706.

Atkinson R., Aschmann S.M., Arey J. & Shorees B., 1992: Formation of OH radicals in the gas phase reaction of O_3 with a series of terpenes. *J. Geophys. Res. 97,* 6065-6073.

Atkinson R. ,1994: Gas-phase tropospheric chemistry of organic compounds. *Journal of physical and chemical reference data. Monograph* 2, 216 pp.

Atkinson R., 2000: Atmospheric chemistry of VOCs and NO_x. *Atmos. Environ*. *34,* 2063-2101.

Bertin N., Staudt M., Hansen U., Seufert G., Ciccioli P., Foster P., Fugit J.-L. & Torres L., 1997: Diurnal and seasonal course of monoterpene emissions from *Quercus Ilex* (L.) under natural conditions - application of light and temperature algorithms. *Atmos. Environ. 31 (S1*), 135-144.

Calogirou A., Larsen B.R., Brussol C., Duane M & Kotzias D., 1996: Decomposition of terpenes by ozone during sampling on Tenax. *Anal. Chem. 68*, 1499-1506.

Calogirou A., Larsen B.R. & Kotzias D., 1999: Gas-phase terpene oxidation products: a review. *Atmos. Environ. 33*, 1423-1439.

Cao X.-L. & Hewitt C.N., 1999: The sampling and analysis of volatile organic compounds in the atmosphere. In: C.N. Hewitt (ed.), *Reactive hydrocarbons in the atmosphere. Academic press, London*, pp. 119-157.

Chameides W. L., Fehsenfeld F., Rodgers M. O., Cardelino C., Martinez J., Parrish D., Lonneman W., Lawson D. R., Rasmussen R. A., Zimmerman P., Greenberg J., Middleton P. & Wang T. ,1992: Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res. 97*, 6037-6055.

Christoffersen T.S., Hjorth J., Horie O., Jensen N.R., Kotzias D., Molander L.L., Neeb P., Ruppert L., Winterhalter R., Virkkula A., Wirtz K. & Larsen B.R., 1998. Cis-Pinic acid, a possible precursor for organic aerosol formation from ozonolysis of α-pinene. *Atmos. Environ. 32*, 1657-1661.

Eberhard J., Müller C., Stocker D.W. & Kerr J.A., 1995: Isomerization of alkoxy radicals under atmospheric conditions. *Environ. Sci. Technol. 29*, 232-241.

Fall R., 1999: Biogenic emissions of volatile organic compounds from higher plants. In: Hewitt C. N. (ed.): *Reactive hydrocarbons in the atmosphere*, Academic Press, London, pp. 43-98.

Finlayson-Pitts B. & Pitts J.N. Jr, 1986: Atmospheric Chemistry: Fundamentals and Experimental Techniques. *John Wiley & Sons*, New York, Chichester, Brisbane, pp 1098.

Fuentes J.D., Lerdau M., Atkinson R., Baldocchi D., Bottenheim J.W., Ciccioli P., Lamb B., Geron C., Gu L., Guenther A., Sharkey T.D. & Stockwell W., 2000: Biogenic hydrocarbons in the atmospheric boundary layer: a review. *Bull. Am. Meteor. Soc. 81*, 1537-1575.

Grinspoon J., Bowman W. D., & Fall R., 1991: Delayed onset of isoprene emission in developing velvet bean (*Mucuna* sp.) leaves. *Plant. Physiol. 97*, 170-174.

Guenther A. B., Monson R. K. & Fall R., 1991: Isoprene and monoterpene emission rate variability: observations with eucalyptus and emission rate algorithm development. *J. Geophys. Res. 96*, 10799-10808.

Guenther A., Zimmerman P.R., Harley P.C., Monson R.K. & Fall R., 1993: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *J. Geophys. Res. 98*, 12609-12617.

Guenther A., Hewitt C. N., Erickson D., Fall R., Geron C., Graedel T., Harley P., Klinger L., Lerdau M., McKay W. A., Pierce T., Scholes B., Steinbrecher R., Tallamraju R., Taylor J., Zimmerman P., 1995: A global model of natural volatile organic compound emissions. *J. Geophys. Res. 100*, 8873-8892.

*Guenther A.*1997: Seasonal and spatial variations in natural volatile organic compound emissions. *Ecol. Appl.* 7, 34-45.

Gölz C., Senzig J. & U. Platt, 2001: NO_3-initiated oxidation of biogenic hydrocarbons. *Chemosphere- Global Change Science 3*, 339-352.

Hallquist M., Wängberg I., Ljungström E., Barnes I. & Becker K.-H., 1999: Aerosol and product yields fromNO_3 radical-initiated oxidation of selected monoterpenes. *Environ. Sci. Technol. 33*, 553-339.

Hari P. & Häkkinen R., 1991: The utilization of old phenological time series of budburst to compare models describing annual cycles of plants. *Tree Physiol. 8*, 281-287.

Harley P., Guenther A. & Zimmerman P., 1997: Environmental controls over isoprene emission in deciduous oak canopies. *Tree Physiol. 17*, 705-714.

Hatakeyama S., Izumi K., Fukuyama T. & Akimoto H., 1989: Reactions of ozone with α-pinene and β-pinene in air: yields of gaseous and particulate products. *J. Geophys. Res. 94*, 13013-13024.

Hatakeyama S., Izumi K., Fukuyama T., Akimoto H. & Washida N., 1991: Reactions of OH with α-pinene and β-pinene in air: estimate of global CO production from the atmospheric oxidation of terpenes. *J. Geophys. Res. 96*, 947-958.

Helmig D. & Arey J., 1992: Organic chemicals in the air at Whitaker's Forest/ Sierra Nevada Mountains, California. *Sci. Tot. Environ. 112,* 233-250.

Hoffmann T., 1995: Adsorptive preconcentration technique including oxidant scavenging for the measurement of reactive natural hydrocarbons in ambient air. *Fresenius J. Anal. Chem. 351*, 41-47.

Hoffmann T., Odum J. R., Bowman F., Collins D., Klockow D., Flagan R. C. & Seinfeld J. H., 1997: Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *J. Atmos. Chem. 26,* 189-222.

Horie O., Neeb P., Limbach P. & Moortgat G.K., 1994: Formation of formic acid and organic peroxides in the ozonolysis of ethene with added water vapour. *Geophys. Res. Lett. 21*, 1523-1526.

Isidorov V.A., 1994: *Volatile emissions of plants: composition, emission rate and ecological significance*. Publ. Dept. of Alga Association, St Petersburg, Russia. ISBN 5-87290-071-1.

Jang M. & Kamens R.M., 1999. Newly characterized products and composition of secondary aerosols from the reaction of α-pinene with ozone. *Atmos. Environ. 33,* 459-474.

Janson W. R., 1993: Monoterpene emissions from Scots Pine and Norwegian Spruce. *J. Geophys. Res. 98*, 2839-2850.

Janson R. & De Serves C., 2001: Acetone and monoterpene emissions from the boreal forest in northern Europe. *Atmos. Environ. 35*, 4629-4637.

Janson R., Rosman K., Karlsson A., & Hansson H.-C., 2001. Biogenic emissions and gaseous precursors to forest aerosols. *Tellus 53B*, 423-440.

Juuti S., Arey J. & Atkinson R.,1990: Monoterpene emission rate measurements from a Monterey Pine. *J. Geophys. Res. 95,* 7515-7519.

Kavouras I.G., Mihalopoulos N. & Stephanou E.G., 1998: Formation of atmospheric particles from organic acids produced by forestes. *Nature 395*, 683-686.

Kesselmeier J. & Staudt M., 1999: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *J. Atmos. Chem. 33*, 23-88.

Kwok E.S. Atkinson R. & Arey J., 1996: Isomerization of β-hydroxyalkoxy radicals formed from the OH radical-initiated reactions of C_4-C_8 1-alkenes. *Environ. Sci. Technol. 30*, 1048-1052.

König G., Brunda M., Puxbaum H., Hewitt C.N., Duckham S.C., Rudolph J., 1995: Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species. *Atmos. Environ. 29,* 861-874.

Lamb B., Guenther A., Gay D. & Westberg H, 1987: A national inventory of biogenic hydrocarbon emissions. *Atmos. Environ. 21*, 1695-1705.

Lappalainen H., 1993: Examples between climate and plant phenology; Examples of plant phenological events in Finland and their relation to effective temperature sum. Licentiate thesis, the University of Helsinki, Dept. of Botany. 115 pp.

Lievonen I. 1982: Chemical compounds in the leaves of birches (in Finnish). M.Sc. thesis, Pharmacognocy Division, Department of Pharmacy, University of Helsinki, Finland.

Lindfors V. & Laurila T., 2000: Biogenic volatile organic compound (VOC) emissions from forests in Finland. *Boreal Env. Res. 5,* 95-113.

Lindfors V., Laurila T., Hakola H., Steinbrecher R. & Rinne J., 2000: Modeling speciated terpenoid emissions from the European boreal forest. *Atmos. Environ. 34,* 4983-4996.

Loreto F. & Sharkey T., 1990: A gas-exchange study of photosynthesis and isoprene emission in *Quercus rubra* L. *Planta 182*, 523-531.

Loreto F., Ciccioli P., Brancaleoni E., Cecinato A., Frattoni M. & Sharkey T., 1996: Different sources of reduced carbon contribute to form three classes of terpenoid emitted by *Quercus ilex* L. leaves. *Proc. Natl. Acad. Sci. USA 93*, 9966-9969.

Monson R., Hills A., Zimmerman P. & Fall R.,1991: Studies of the relationship between isoprene emission rate and CO2 or photon-flux density using real time isoprene analyzer. *Plant Cell Environ. 14*, 517-523.

Monson R. K., Harley P. C., Litvak M. E., Wildermuth M., Guenther A. B., Zimmerman P. R. & Fall R., 1994: Environmental and developmental controls over the seasonal pattern of isoprene emission from aspen leaves. *Oecologia 99*, 260-270.

Mroueh U.-M. ,1994: Inventory of volatile organic compound (VOC) emissions (1993) *Technical Research Centre of Finland, VTT-Research Notes 1609,* pp 29 (in Finnish).

Muthuramu K., Shepson P.B. & O'Brien J.M., 1993: Preparation, analysis and atmospheric production of multifunctional organic nitrates. *Environ. Sci. Technol. 27,* 1117-1124.

Müller J.-F., 1992: Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases. *J. Geophys. Res. 97*, 3787-3804.

Mäkelä J.M., Aalto P., Jokinen V., Pohja T., Nissinen A., Palmroth S., Markkanen T., Seitsonen K., Lihavainen H. & Kulmala M., 1997: Observations of ultrafine particle formation and growth in boreal forest. *Geophys. Res. Lett. 24*, 1219-1222.

National Research Council, 1991: Rethinking the ozone problem in urban and regional air pollution. *National Academy Press,* Washington D.C., pp. 500.

Neeb P., Sauer F., Horie O. & Moortgat G.K., 1997: Formation of hydroxymethyl hydroperoxide and formic acids in alkene ozonolysis in the presence of water vapour. *Atmos. Environ. 31,* 1417-1423.

Noziére B., Barnes I. & Becker K.-H., 1999: Product study and mechanisms of the reactions of α-pinene and pinonaldehyde with OH radicals. *J. Geophys. Res. 104,* 23645-23656.

Paulson S.E. & Seinfeld J.H., 1992: Atmospheric photochemical oxidation of 1-octene: OH, O_3, and $O(^3P)$ reactions. *Environ. Sci. Technol. 26, 1165-1173.*

Paulson S.E., Chung M., Sen A.D. & Orzechowska G., 1998: Measurement of OH radical formation from the reaction of ozone with several biogenic alkenes. *J. Geophys. Res. 103*, 25533-25539.

Pétron G., Harley P., Greenberg J. & Guenther A., 2001: Seasonal temperature variations influence isoprene emission. *Geophys. Res. Lett. 28*, 1707-1710.

Rinne J., Hakola H. & Laurila T., 1999: Vertical fluxes of monoterpenes above a Scots pine stand in the boreal vegetation zone. *Phys. Chem. Earth V 24,* 711-715.

Rinne J., Hakola H., Laurila T. & Rannik Ü., 2000 a: Canopy scale monoterpene emissions of *Pinus sylvestris* dominated forests. *Atmos. Environ. 34*, 1099-1107.

Rinne J., Tuovinen J.-P., Laurila T., Hakola H., Aurela M. & Hypén H., 2000 b: Measurements of hydrocarbon fluxes by a gradient method above a northern boreal forest. *Agric. For. Meteorol. 102*, 25-37.

Schuh G., Heiden A.C., Hoffmann Th., Kahl J., Rockel P., Rudolph J. & Wildt J., 1997: Emissions of volatile organic compounds from sunflower and beech: Dependence on temperature and light intensity. *J. Atmos. Chem. 27*, 291-318.

Schürmann W., Ziegler H., Kotzias D., Schönwitz R. & Steinbrecher R., 1993: Emission of biosynthesized monoterpenes from needles of Norway spruce. *Naturwissenschaften, 80*, 276-278.

Shu Y. & Atkinson R., 1995: Atmospheric lifetimes and fates of a series of sesquiterpenes. *J. Geophys. Res. 100*, 7275-7281.

Singsaas E.L., Lerdau M., Winter K., & Sharkey T., 1997: Isoprene increases thermotolerance of isoprene-emitting species. *Plant Physiol. 115*, 1413-1420.

Skov H., Hjoth J., Lohse C., Jensen N.R. & Restelli G., 1992: Products and mechanisms of the reactions of the nitrate radical (NO_3) with isoprene, 1,3-butadiene and 2,3-dimethyl-1,3-butadiene in air. *Atmos. Environ. 26A*, 2771-2783.

Spanke J., Rannik Ü. Forkel R., Nigge W. & Hoffmann T., 2001: Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: filed measurements and modelling. *Tellus 53B*, 406-422.

Staudt M., Bertin N., Hansen U., Seufert G., Ciccioli P., Foster P., Frenzel B., Fugit J.-L., 1997: Seasonal and diurnal patterns of monoterpene emissions from Pinus pinea (L.) under field conditions. *Atmos. Environ. 31 (S1)*, 145-156.

Staudt M., Bertin N., Frenzel B., Seufert G., 2000: Seasonal variation in amount and composition of monoterpenes emitted by young *Pinus pinea* trees – Implications for emission modelling. *J. Atmos. Chem. 35*, 77-99.

Tingey D.T., Manning M., Grothaus L.C., & Burns W., 1980: Influence of light and temperature on monoterpene emission rates from slash pine. *Plant Physiol. 65*, 797-801.

Vinckier C., Compernolle F., Saleh A.M., Van Hoof N. & Van Hees I., 1998: Product yields of the α-pinene rection with hydroxyl radicals and the implication on the global emission of trace compounds in the atmosphere. *Fresenius Envir. Bull. 7*, 361-368.

Wayne R.P., Barnes I., Biggs P., Burrows J.P., Canosa-Mas C.E., Hjorth J., LeBras G., Moortgat G.K., Perner D., Poulet G., Restelli G., & Sidebottom H., 1991: The nitrate radical: physics, chemistry and the atmosphere. *Atmos. Environ. 25A*, 1-203.

Wiener A. M., Arey J., Atkinson R., Aschmann S.M., Long W.D., Morrison L. & Olszyk D.M., 1992: Emission rates of organics from vegetation in California's Central Valley. *Atmos. Environ. 26A*, 2647-2659.

Wängberg I., Barnes I., & Becker K.H., 1997: Product and mechanistic study of the reaction of NO_3 radicals with α-pinene. *Environ. Sci. Technol.* 31, 2130-2135.

Yokouchi Y. & Ambe Y., 1984: Factors affecting the emission of monoterpenes from red pine (*Pinus densiflora*). *Plant Physiol. 75*, 1009-1012.

Yu J., Griffin R.J., Cocker III D.R., Flagan R.C., Seinfeld J.H. & Blanchard P., 1999: Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. *Geophys. Res. Lett. 26*, 1145-1148.

Zielinska B., Sagebiel J.C., Harshfield G., Gertler A.W. & Pierson W.R., 1996: Volatile organic compounds up to C_{20} emitted from vehicles; measurement methods. *Atmos. Environ. 30*, 2269-2286.